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JOURNAL

OF

THE CHEMICAL SOCIETY.

ABSTRACTS OF CHEMICAL PAPERS PUBLISHED IN
BRITISH AND FOREIGN JOURNALS.

PART I.

Organic Chemistry.

Elementary Composition of the Mineral Oils. By CARL ENGLER and L. JEZIORANSKI (*Ber.*, 1895, **28**, 2501—2505).—The authors have made analyses of samples of oil from Galicia, Sumatra, Baku (Bibi-Eibat), Alsace (Pechelbronn), and Pennsylvania, and also of the various fractions obtained from these oils, namely, below 150°, 150—200°, residue. From the analyses, and from the amount of each fraction absorbed by concentrated sulphuric acid, the authors conclude that the lower fractions consist mainly of saturated hydrocarbons of the paraffin series, except in the case of the Baku oil, whereas the portion boiling above 200° consists, in all cases, mainly of unsaturated hydrocarbons of the olefine series. J. J. S.

Fractional Distillation applied to American Petroleum and Russian Kerosene. By J. ALFRED WANKLYN and WILLIAM J. COOPER (*Phil. Mag.*, 1895, [5], **40**, 225—228).—The paper contains the results of the authors' experiments on the fractional distillation of American petroleum, and the vapour density, specific gravity, and composition of the various fractions, the results being compared with those obtained by the authors in the case of Russian kerosene. They consider that each of these petroleum contains a homologous series of hydrocarbons with a common increment of 7, instead of 14, a result that would require the accepted atomic weight of carbon to be halved. For a like carbon contents, the hydrocarbons of the Russian series, which contain 2 atoms of hydrogen less per molecule, always show a slightly greater specific gravity, the increment varying from 0.025 to 0.035. L. M. J.

Russian Kerosene. By J. ALFRED WANKLYN and WILLIAM J. COOPER (*Chem. News*, 1895, **72**, 7).—A tabular *résumé* is given of the work done on the hydrocarbons existing in commercial Russian kerosene (Abstr., 1895, i, 77 and 437). D. A. L.

Hexylene and Hexylic Hydride derived from Mannitol by Reduction with Hydriodic acid. By J. ALFRED WANKLYN (*Chem. News*, 1895, **72**, 75).—The specific gravity of hexylene at 0° is given as 0.7017, and of hexylic hydride at 0° as 0.6759, differing by 0.0258. A similar difference, of 0.025 to 0.035, is observed between the densities of the hydrocarbons of the same carbon condensation obtained from Russian and American petroleum respectively, the former being the denser. D. A. L.

Unsaturated Hydrocarbons. By ALEXANDRE DESGREZ (*Ann. Chim. Phys.*, 1894, [7], **3**, 209—246).—Berthelot (*Ann. Chim. Phys.*, [3], **43**, 385, and [5], **23**, 184) has shown that unsaturated hydrocarbons can be made to combine with the elements of water indirectly by means of sulphuric acid; and Béhal and Desgrez (Abstr., 1892, 1162) have shown that unsaturated hydrocarbons also unite with the elements of acetic acid at a fairly high temperature to form ethereal salts. The author now demonstrates that the elements of water can be directly added to the hydrocarbons of the acetylene series. For this purpose, the hydrocarbon is placed with water in iron tubes, enamelled inside, and heated in a bath of sodium and potassium nitrates. Instead of acetylene, the author has used acetylenedicarboxylic acid, and finds that, when the acid and water are heated at 315° for 20 minutes, a quantity of paraldehyde is formed. Tetrolic acid, when heated with water in a similar manner, gives rise to acetone.

Enanthylidene, with water at 325°, yields methyl amyl ketone. Caprylidene, when heated with water for three hours at 320—330°, yields methyl hexyl ketone. Phenylacetylene, under similar conditions, gives acetophenone; methylbutylacetylene yields a mixture of equal quantities of methyl amyl ketone and *ethyl butyl ketone*. The ketone distils at 146—147°, and does not unite with sodium hydrogen sulphite. A number of experiments were made with methylamylacetylene and water, from which the author concludes that the yield of ketone increases with the period of heating, that a maximum is reached with a period of three hours, from which point the yield again decreases, and, further, that the yield increases with the temperature, reaching a maximum of 75 per cent. of the theoretical at 360°. The product consists of a mixture of methylamylacetone and *ethyl butyl ketone*.

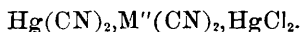
Diphenylacetylene (tolane), under similar conditions, yields deoxybenzoin, which can be separated from the unaltered tolane by means of alcohol.

It is finally shown that the above hydrocarbons contained no trace of hydrogen chloride, which might act as a condensing agent, and, therefore, the general reaction given above shows a direct synthesis of ketones from the unsaturated hydrocarbons of the acetylene series.

J. J. S.

Compounds of Mercuric Cyanide with Metallic Chlorides.

By **RAOUL VARET** (*Compt. rend.*, 1895, **121**, 348—351).—Experiments were made with the view of ascertaining whether compounds of the type $2\text{Hg}(\text{CN})_2, \text{M}''\text{Cl}_2 + n\text{H}_2\text{O}$ have really this constitution, or are compounds of a double cyanide and mercuric chloride,



The first column contains the heat of dissolution of the crystallised salt; the second column the heat developed by mixing dilute solutions of mercuric cyanide and the metallic chloride; the third column the heat of formation of the solid double salt from solid mercuric cyanide, the solid metallic chloride and liquid water.

	I.	II.	III.
$2\text{Hg}(\text{CN})_2, 2\text{NaCl} + 2\frac{1}{2}\text{H}_2\text{O} \dots\dots$	-16.20 Cal.	+0.33 Cal.	+ 7.95 Cal.
$2\text{Hg}(\text{CN})_2, 2\text{NH}_4\text{Cl} + 1\frac{1}{2}\text{H}_2\text{O} \dots\dots$	-14.80 „	+0.38 „	+ 1.18 „
$2\text{Hg}(\text{CN})_2, \text{BaCl}_2 + 5\text{H}_2\text{O} \dots\dots$	-17.1 „	+0.45 „	+13.55 „
$2\text{Hg}(\text{CN})_2, \text{SrCl}_2 + 6\text{H}_2\text{O} \dots\dots$	-15.80 „	+0.45 „	+21.25 „
$2\text{Hg}(\text{CN})_2, \text{CaCl}_2 + 6\text{H}_2\text{O} \dots\dots$	-14.20 „	+0.50 „	+26.1 „
$2\text{Hg}(\text{CN})_2, \text{MgCl}_2 + 6\text{H}_2\text{O} \dots\dots$	- 9.9 „	+0.50 „	+40.4 „
$2\text{Hg}(\text{CN})_2, \text{ZnCl}_2 + 7\text{H}_2\text{O} \dots\dots$	-13.30 „	+0.90 „	+23.8 „
$\text{Hg}(\text{CN})_2, \text{CdCl}_2 + 2\text{H}_2\text{O} \dots\dots$	- 9.30 „	+0.38 „	+ 6.48 „

These results indicate that the whole of the cyanogen remains in direct combination with the mercury, and this view is supported by the fact that the cold solutions of the double salts are not alkaline to litmus, and, if heated at 30° with a soluble picrate, no isopurpurate is formed. If, however, the solutions are boiled, they become slightly alkaline, and give the isopurpurate reaction, from which it follows that, at the higher temperature, there is a migration of atoms, and part of the cyanogen becomes combined with the alkali or alkaline-earth metal.

C. H. B.

Copper Ferrocyanide. By **GUSTAV RAUTER** (*Zeit. angew. Chem.*, 1895, 315—316).—This is an investigation of the nature of the precipitate formed, under varying conditions, by the interaction of copper sulphate and potassium ferrocyanide.

The upshot is that the precipitate always retains potassium ferrocyanide, but that this must not be looked on as a chemical constituent but only as an impurity. Owing to the great difficulty experienced in completely washing the voluminous deposit, a certain amount of potash is obstinately retained.

L. DE K.

Sulphur as a Preservative of Chloroform. By **L. ALLAIN** (*J. Pharm.*, 1895, [6], **2**, 252—255).—Chloroform, saturated with sulphur in the cold, may be kept in direct sunlight for months, without undergoing change; in particular, no carbonyl chloride is formed. This stability is not due to any change produced by the sulphur, for the redistilled liquid rapidly decomposes when exposed to the same

conditions. As the anæsthetic properties of the chloroform are not modified by the presence of the sulphur, the addition of this preservative is to be recommended. JN. W.

Nitro-alcohols. By LOUIS HENRY (*Compt. rend.*, 1895, **121**, 210—213).—Nitromethane and formaldehyde, in presence of a small quantity of potassium carbonate, react quantitatively with production of *tertiary nitrotrihydroxybutane*, $\text{NO}_2\cdot\text{C}(\text{CH}_2\cdot\text{OH})_3$, a white, solid compound, which crystallises in needles or in large prisms melting at 158 — 159° , and soluble in water, alcohols, and acetone, but less soluble in ether. Attempts to obtain products of the interaction of one molecule of nitromethane and one and two molecules respectively of formaldehyde were unsuccessful.

Nitroethane and formaldehyde, in presence of potassium carbonate, yield the compound $\text{NO}_2\cdot\text{CMe}(\text{CH}_2\cdot\text{OH})_2$, which is *tertiary nitrotrihydroxybutane* or *tertiary nitroisobutylene glycol*. It crystallises very readily, melts at 139 — 140° , and is soluble in water, alcohols, and acetone, but less soluble in ether. Secondary nitropropane and formaldehyde, under similar conditions, yield the nitroisobutylic alcohol, $\text{NO}_2\cdot\text{CMe}_2\cdot\text{CH}_2\cdot\text{OH}$, which melts at 82° , crystallises very readily, is very soluble in alcohols and acetone, but less soluble in water, and more soluble in ether than the two preceding compounds.

From these results it follows that the reaction capacities of the three nitroparaffins with respect to formaldehyde are proportional to the number of hydrogen atoms attached to the group $\text{C}\cdot\text{NO}_2$, and there is little doubt that tertiary nitrobutane, $\text{NO}_2\cdot\text{CMe}_3$, would have no action on formaldehyde or the other aldehydes of the same series.

C. H. B.

Glucoseacetone. By EMIL FISCHER (*Ber.*, 1895, **28**, 2496—2497).—The author has previously shown (*Abstr.*, 1895, i, 440) that *d*-glucose, arabinose, and fructose react with two molecules of acetone, and rhamnose with only one; it is now shown that glucose can also form a condensation product with one molecule of acetone. This substance has the composition $\text{C}_6\text{H}_{10}\text{O}_6\cdot\text{CMe}_2$, and the author terms it *glucose-acetone*. It differs from the alcoholic glucosides in the fact that it is not acted on by emulsin or by the enzyme of yeast; it forms small, felted needles, melts at 160 — 161° (corr.), is soluble in water, and is lævorotatory. It has a bitter taste, does not sublime at 100° , but may be distilled in small quantities without undergoing decomposition; it is readily decomposed by dilute acids, but has no action on Fehling's solution. J. J. S.

Inversion of Maltose and Isomaltose by means of Yeast. By CARL J. LINTNER (*Chem. Centr.*, 1895, i, 271—272; from *Zeit. Ges. Brauw.*, **17**, 414—415).—Referring to the investigations of E. Fischer on the influence of the configuration of the molecule on the action of enzymes, the author has observed that the hydrolysis of maltose proceeds most rapidly with yeast powder, the aqueous extract is less active, and precipitated invertin least. Isomaltose is more readily attacked than maltose. The enzyme is less soluble than invertin, and appears

to be more closely allied to the glycolytic ferments. The presence of dextrose in small quantity in Munich lager beer, is due to the action of yeast on isomaltose. J. B. T.

The Inulin of Garlic, Hyacinth, Narcissus, and Tuberose.

By R. CHEVASTELON (*J. Pharm.*, 1895, [6], 2, 83—86; from *Inaug. Diss.*, Paris, 1894).—The reserve material of the bulbs and other underground parts of certain monocotyledons is a kind of inulin. To separate this substance, the bulbs, &c., are cut into small fragments, and digested with ether, to cause the expulsion of the sap from the cells; the sap collecting at the bottom of the vessel, together with a further amount remaining in the fragments, and liberated by pressure, is purified with basic lead acetate and animal charcoal, and the inulin precipitated by baryta water. The insoluble baryta compound of the carbohydrate is decomposed by carbonic anhydride, and the inulin precipitated with alcohol-ether as a syrup. Finally, this is dried in succession by washing with alcohol and ether, and then under diminished pressure, and at 100°.

The *inulin of garlic*, $C_6H_{10}O_5$, is a white, inodorous, amorphous powder, distinct from the inulin of the Jerusalem artichoke. Its taste is insipid, and it is very deliquescent. It melts at 175—176°, and is soluble in water and dilute alcohol, but only sparingly in strong alcohol. The rotatory power is $[\alpha]_D = -39^\circ$.

It does not reduce alkaline copper tartrate, and is completely hydrolysed by acids to levulose. It is precipitated neither by normal nor by basic lead acetate, except in presence of ammonia. It is not hydrolysed by amylase (malt diastase), but is resolved into levulose by an enzyme *inulase*, which is secreted by *Aspergillus niger*, and is similar to the enzyme of the inulin of the Jerusalem artichoke, and of *Atractylis*. The inulin of garlic is not fermented either by hydrolytic or non-hydrolytic yeasts.

The sap from the offshoots of the garlic bulbs contains only traces of reducing sugars, and yields nothing but levulose on hydrolysis, so that it contains no reserve material but inulin.

The inulin of the sap of the bulbs of various species of hyacinth is identical with that from garlic. The bulbs also contain a small amount of levulose, and a large amount of starch, so that here the reserve material is stored in both soluble and insoluble forms.

The inulin from the bulbs of the narcissus and tuberose is also identical with that from garlic; neither of these contains starch, but the narcissus sap contains both glucose and levulose, whilst that of the tuberose contains glucose only.

Various other bulbous monocotyledons were examined, such as the onion, tulip, and iris. JN. W.

Glyoxylic acid and its Behaviour towards Carbohydrates.

By CARL BOETTINGER (*Arch. Pharm.*, 1895, 233, 287—294).—Glyoxylic acid acts as a hydrolysing agent towards starch and cane sugar, and it prevents the fermentation of the products formed, for it acts on yeast as a poison. From glyoxylic acid and glucose, a syrup is obtained, which is asserted to have the constant composition

$C_6H_{12}O_6, C_2H_2O_3 + H_2O$; with galactose a similar compound may have been obtained, and with levulose a compound $C_6H_{12}O_6, 2C_2H_3O_2$.

C. F. B.

Preparation of Glycogen. By D. HUIZINGA (*Pflüger's Archiv*, 1895, **61**, 32—38).—On account of the opalescence of glycogen solutions, the presence of albumoses in small quantity can only be ascertained by means of the biuret reaction or by Millon's reagent; with the former, not less than 0.5 per cent. can be detected; with the latter, a distinct orange colour is obtained when the solution contains 0.1 per cent.; if the albumose is precipitated by means of a solution containing sodium tungstate (100 parts), phosphoric acid (50 parts), concentrated hydrochloric acid (10 parts), and water (500 parts), and the dried precipitate treated with Millon's reagent, the presence of 0.02 per cent. of albumose may be distinctly recognised. The above experiments were made with albumose prepared from egg albumin; the presence of glycogen is without effect on the reactions. The boiling water usually employed for the preparation of glycogen extracts albumoses in considerable quantity, and their subsequent separation is attended with considerable difficulty; trichloroacetic acid, which Fränkel used instead of water, also dissolves albumoses, as do sulphosalicylic acid and formaldehyde solutions; saturated solution of mercuric chloride extracts pure glycogen, but the resulting liquid is often unsuitable for filtration; the best results were obtained by the use of equal parts of saturated solution of mercuric chloride and Esbach's reagent, made by dissolving picric acid (10 grams) and citric acid (20 grams) in water (1 litre). The glycogen, after washing with alcohol and ether-alcohol, was free from albumoses, and contained 0.62—0.80 per cent. of ash. This method, although good for the preparation of glycogen, is not adapted for its quantitative estimation, as it yielded only 78—89 per cent. of the total glycogen determined by Külz's method.

J. B. T.

Oxycellulose. By R. W. TROMP DE HAAS and BERNHARD TOLLENS (*Annalen*, 1895, **286**, 296—300; compare Abstr., 1893, i, 295).—The authors have hydrolysed, with sulphuric acid, oxycellulose obtained by treating fir saw-dust with nitric acid. Twenty grams of oxycellulose was added slowly to 100 grams of concentrated sulphuric acid mixed with 20 grams of water, 80 grams of water being added after an hour; on the following morning, 2.5 litres of water were added to the liquid, which was heated in a reflux apparatus for five hours in boiling water. After neutralising the pale yellow liquid with calcium carbonate, the filtered solution yielded 3 grams of dextrose, having the specific rotatory power $[\alpha]_D = +51.2^\circ$. Determination of cellulose by Lange's method indicated the presence of about 20 per cent., whilst 3 per cent. of furfuraldehyde was obtained from the oxycellulose by distillation with hydrochloric acid.

From these results, the authors conclude that the oxycellulose obtained from fir-wood is not identical with the oxycelluloses investigated by Cross and Bevan, Witz, and Nastjukoff.

M. O. F.

Remarks on the Foregoing Paper. By BERNHARD TOLLENS (*Annalen*, 1895, **286**, 301—302).—Many substances which yield furfuraldehyde when distilled with hydrochloric acid are found to contain, in some form, pentoses or glycuronic acid. This is not the case with the oxycellulose described in the foregoing abstract, and the author suggests glycoson, $C_6H_{10}O_6$, as a possible source of the production of furfuraldehyde from this substance. M. O. F.

Constitution of Pectin Substances. By BERNHARD TOLLENS (*Annalen*, **286**, 292—295).—From a consideration of the properties of these substances and the products of their hydrolysis, the author regards them as carbohydrates combined chemically with acids, this view having been already advanced by O'Sullivan regarding the vegetable gums. M. O. F.

Pectin Substances. By R. W. TROMP DE HAAS and BERNHARD TOLLENS (*Annalen*, 1895, **286**, 278—292).—Many attempts have been made to establish a relationship between pectins and vegetable gums (carbohydrates). Accurate determinations of composition are essential to generalisations of this character, and the authors have accordingly prepared and analysed pectin substances from various sources, the proportion between hydrogen and oxygen being indicated in each case. The pectins were precipitated by alcohol in the juice expressed from the fruits, and, after being washed with ether, were dried over sulphuric acid.

The analytical results are embodied in the following table.

Pectin.	Percentage of C.	Ratio of H to O.	Percentage of Ash.
Apple A	43·35	1 : 7·9	5·95
Apple B	43·46	1 : 7·4	6·54
Cherry	42·42	1 : 7·7	20·50
Rhubarb A	43·31	1 : 7·3	4·19
Rhubarb B	42·89	1 : 8·9	6·88
Currant	46·87	1 : 8·5	5·02
Plum	42·92	1 : 8·5	3·34
Swede A	41·08	1 : 9·0	7·29
Swede B	42·33	1 : 8·8	1·97

From this it is clear that the pectins are allied in composition to the carbohydrates, and that the low proportion of hydrogen to oxygen (1 : 10—12) recorded by previous observers is not confirmed.

Hydrolysis of these pectins leads to the formation of hexoses or pentoses. M. O. F.

Preparation of Methylamine. By ANDRÉ BROCHET and R. CAMBIER (*J. Pharm.*, 1895, [6], **2**, 172—173; from *Rev. Chim. Industr.*, June, 1895; compare Abstr., 1895, i, 642).—Formaldehyde (20 kilos. of 40 per cent.) is distilled with ammonium chloride (10 kilos.). The action commences at 40°, when methylal passes over, and the distillate up to 95° contains 60—79 per cent. of that substance. The

residue is evaporated down until ammonium chloride commences to crystallise out, and, on cooling, the whole excess of that substance separates. The liquid remaining is a nearly pure solution of methylamine hydrochloride, from which the pure substance is obtained by evaporation under low pressure and recrystallisation from alcohol. The yield of 95 per cent. methylamine hydrochloride, melting at 210° , is 8.5 kilos. with the above quantities, and, at the same time, 3.8 kilos. of methylal and 2.2 kilos. of carbonic anhydride are formed, and 3.5 kilos. of ammonium chloride recovered unchanged. JX. W.

Chloro-derivatives of Amines. By ARMAND BERG (*Ann. Chim. Phys.*, 1895, [7], 3, 289—361).—The normal butylamines have been prepared according to Hofmann's method by the action of butylic chloride on a dilute alcoholic solution of ammonia. The bases are first separated by means of their hydrochlorides, and then the primary base is purified by conversion into *dibutylloxamide*, $C_2O_2(NHC_4H_9)_2$, which melts at 153° , and is but sparingly soluble in water. The mother liquor contains *butylamine butylloxamate*, $C_4H_9NH\cdot CO\cdot COO\cdot NH_2\cdot C_4H_9$, which, when heated in aqueous solution with calcium chloride, yields *calcium butylloxamate*,



Butylamine oxalate, $C_2O_2(ONH_2\cdot C_4H_9)_2$, is deposited on evaporating the mother liquid of the oxamate.

Dibutylamine hydrochloride is made use of in the separation of the secondary base. The *aurochloride*, $NH_2(C_4H_9)_2AuCl_4$, is precipitated when concentrated solutions of gold chloride and dibutylamine hydrochloride are mixed; it crystallises in long, golden needles, and melts at 170° . The *stannichloride*, $2NH_2(C_4H_9)_2Cl\cdot SnCl_4 + H_2O$, crystallises in long, colourless needles. Dibutylamine hydrogen oxalate, $COOH\cdot COO\cdot NH_2(C_4H_9)_2$, is much more readily soluble in water than the corresponding diisobutylamine salt. *Dibutylamine picrate* melts at 59.5° .

The tributylamine hydrochloride is extremely deliquescent. The *picrate* melts at 100.5° , and is very sparingly soluble in water.

The isobutylamines have been prepared by a similar method; the author finds that when a mixture of isobutylic chloride (1 mol.) and aqueous ammonia (1 mol.), to which just sufficient alcohol for solution has been added, is heated at 110 — 115° , the primary base is the chief product. It may be purified by conversion into the oxamide (Malbot, *Abstr.*, 1891, 817). The pure base boils at 67.9 — 68° . (Reimer gives 62 — 65° , and Perkin 68 — 69° .) The secondary and tertiary bases are best separated by conversion into the acid oxalates. Diisobutylamine boils at 140.6 — 140.8° . (Reimer gives 122 — 125° , Malbot 137° , and Perkin 139 — 140° .)

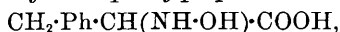
The amylamines have been prepared and separated by similar methods. *Amylamine amyloxamate*, $C_5H_{11}\cdot NH\cdot CO\cdot COO\cdot NH_2\cdot C_5H_{11} + H_2O$, crystallises in colourless needles, and is readily soluble in hot water. *Calcium amyloxamate*, $(C_5H_{11}\cdot NH\cdot CO\cdot COO)_2Ca + H_2O$, is sparingly soluble in cold water, readily in boiling, and crystallises in slender, colourless needles.

Most of the chloramines have been described before (Abstr., 1890, 952; 1892, 804 and 1172; 1893, i, 296 and 497). The monochloramines were prepared by the action of a concentrated solution of sodium hypochlorite on an aqueous solution of the hydrochloride of the amine. The dichloramines were prepared by Tcherniak's method.

Butylchloramine, $C_4H_9 \cdot NHCl$, is a faintly yellowish oil, has a sharp odour, is insoluble in water, decomposes on heating, and has a sp. gr. of 0.992 at 0° . *Butyldichloramine*, $C_4H_9 \cdot NCl_2$, is a yellow liquid, with a sp. gr. = 1.112 at 0° . It boils at 71° under a pressure of 80 mm. *Dibutylchloramine*, $(C_4H_9)_2NCl$, is an oily liquid with a sp. gr. of 0.906 at 0° , and boils at 99° under a pressure of 52 mm.; it slowly decomposes when kept. These chloramines undergo decompositions similar to those given for the chloramines which have been previously described; thus when acted on by reducing agents they are converted into the hydrochlorides of the corresponding bases. Quinol, pyrogallol, and gallic acid give colorations with the chloramines. Sulphuric acid acts on the monochloramines, converting them into the base and the corresponding dichloramines. Amylchloramine and silver nitrite act in the presence of alcohol, forming the silver derivative of amylnitramine, which crystallises in fine tablets.

The reactions with potassium iodide and potassium cyanide are similar to those previously described. J. J. S.

Constitution of the Isonitramines. By WILHELM TRAUBE (*Ber.*, 1895, **28**, 2297—2302; compare Abstr., 1895, i, 592).—The isonitraminic acids are converted, by boiling with dilute hydrochloric acid, into the corresponding amidoxylic acids, which may be reconverted into the isonitraminic acids by the action of nitrous acid. *Hydroxyl-amidoacetic acid*, $HO \cdot NH \cdot CH_2 \cdot COOH$, crystallises in lustrous, rhombic tablets melting at 135° , and reduces Fehling's solution at the ordinary temperature. *Hydroxylamidophenylpropionic acid*,



crystallises in prisms melting at 157 — 158° . When this acid is treated with nitrous acid, it yields isonitraminephenylpropionic acid, identical with that prepared from ethylic benzylacetoacetate and nitric oxide, along with another substance which has the formula C_8H_8NO . This second compound does not reduce Fehling's solution, and explodes when heated.

The isonitraminic acids probably have the constitution $R \cdot N < \begin{smallmatrix} NOH \\ O \end{smallmatrix}$, since they are formed by the action of nitrous acid on the amidoxylic acids. A. H.

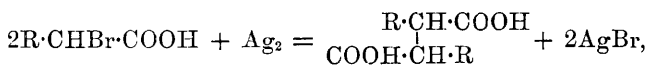
Existence of Imido-ethers derived from Hydrocyanic acid. By ADOLF PINNER (*Ber.*, 1895, **28**, 2454—2458).—A reply to the criticisms of J. U. Nef (*Annalen*, 1895, **287**, 328). Nef has stated that the substance, previously described by the author as the hydrochloride of the ethylic ether of formimide, $NH \cdot CH \cdot OEt, HCl$, is a mixture of five different compounds. In this paper reasons are given why it should still be considered a homogeneous substance. J. J. S.

Condensation of Isovaleraldehyde. By L. KOHN (*Compt. rend.*, 1895, **121**, 259—260).—Isovaleraldehyde and potassium hydroxide do not yield secondary glycols analogous to those obtained by Fosseck from isobutaldehyde, but two products are formed. One boils at 82° under a pressure of 15 mm., or 187° under 746 mm., and oxidises very easily with formation of an acid, $C_{10}H_{18}O_2$. The other boils at 140° under a pressure of 18 mm., and seems to be a polymeride of valeral.

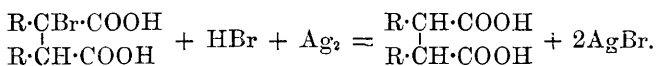
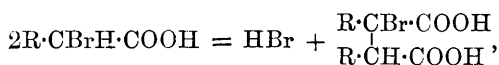
C. H. B.

Action of finely divided Silver on Halogen Derivatives of Aliphatic acids. By CARL HELL (*Ber.*, 1895, **28**, 2439—2445; compare J. Wislicenus, *Annalen*, **149**, 215; Hell, *Ber.*, **6**, 28; **7**, 319; **10**, 2229; **13**, 473; **22**, 48).—The author considers that the general equations previously given by him to represent the action of finely divided silver on the halogen derivatives of the fatty acids do not account for the formation of many of the compounds obtained in the reaction. It is now suggested that in the formation of dicarboxylic acids from α -halogen (*e.g.* bromine) derivatives of the fatty acids, two reactions occur: (1) the bromine atoms are removed by the silver, and the two residues then unite to form a dicarboxylic acid; (2) hydrogen bromide is removed by the union of the bromine of 1 mol. with a hydrogen atom in the α -position to the bromine of a second molecule.

The author considers that this accounts for the formation of tetramethylsuccinic and trimethylglutaric acids from bromisobutyric acid, and that it also accounts for the formation of both stereoisomeric dialkylsuccinic acids by similar methods. Thus by reaction (1) we obtain one modification,



and by reaction (2) we obtain the second modification—



A third reaction, which often occurs simultaneously, is the removal of hydrogen bromide from 1 mol., and the formation of an unsaturated acid of the acrylic series. The formation of pyrocinnonic acid from α -bromopropionic acid and silver is probably due to a similar reaction.

J. J. S.

Electrolytic Synthesis of Monocarboxylic acids of the Fatty Series. By WILHELM VON MILLER and HANS HOFER (*Ber.*, 1895, **28**, 2427—2439; compare *Abstr.*, 1894, i, 228).—The authors have made electrolytic experiments with mixtures of potassium acetate and potassium ethylic succinate in Hofer's apparatus (*Ber.*, **27**, 464).

They show that when a solution of potassium ethylic succinate is

used as the positive electrolyte, and a concentrated solution of potassium carbonate (kept neutral by passing in carbonic anhydride) as the negative, theoretical yields of ethylic adipate may be obtained; whereas Crum-Brown and Walker by their method obtained a yield of only 35 per cent. (Abstr., 1891, 1192; 1893, i, 394). If a mixture of potassium acetate and potassium ethylic succinate is used as the positive electrolyte, and the negative is the same as in the previous case, a yield of 40–69 per cent. of ethylic butyrate can be obtained. A small quantity of the adipate is formed at the same time, this amount varying with the composition of the original mixture used.

By replacing the potassium acetate by potassium propionate, butyrate, and isobutyrate respectively, the authors have succeeded in synthesising ethylic valerate, caproate, and isobutylacetate.

The gases evolved during the electrolysis were examined in each case. They contain carbonic anhydride (73–82 per cent.), oxygen (0.3–0.4 per cent.), carbonic oxide (1–3 per cent.).

It has also been found possible to obtain ethylic iodide, together with iodoform and sodium iodate, by the electrolysis of a solution containing sodium propionate as the positive electrolyte and potassium iodide as the negative. With potassium succinate as the positive, β -iodopropionic acid is obtained. When sodium propionate and potassium nitrite were used as the two electrolytes, a small quantity of nitroethane was obtained; and when potassium acetate and potassium glycolate were used, the authors obtained formaldehyde at the negative pole and ethylic alcohol at the positive.

Similar experiments with a mixture of potassium ethylic malonate and potassium acetate at the positive pole, and potassium carbonate at the negative, gave ethylic propionate as the chief product; but with a mixture of potassium ethylic malonate and potassium propionate at the positive pole, ethylic valerate was formed, and similarly with a mixture of the malonate and potassium butyrate, ethylic valerate was the chief product.

J. J. S.

β -Hydroxy- α -dimethylisocaproic acid and Diisopropylglycollic acid. By ALEXANDER BARYLOWITSCH (*Ber.*, 1895, 28, 2463–2466).—Reformatsky has obtained β -hydroxy- α -dimethylisocaproic acid, $\text{CHMe}_2\cdot\text{CH}(\text{OH})\cdot\text{CMe}_2\cdot\text{COOH}$, by the action of zinc and ethylic bromisobutyrate on isobutaldehyde. This acid melts at 92° , whereas the acid described by Wohlbrück and Hantzsch under the same name melts at 111 – 112° . The author has further investigated the acid of Wohlbrück-Hantzsch (Abstr., 1887, 1099), and finds that it is not β -hydroxy- α -dimethylisocaproic acid, but is identical with the diisopropylglycollic acid, $\text{OH}\cdot\text{C}(\text{CHMe}_2)_2\cdot\text{COOH}$, previously described by Markovnikoff.

J. J. S.

Glucic acid (?). By HEINRICH WINTER (*Chem. Centr.*, 1895, i, 371–372; from *Z. Ver. Rübenzuck*, 1894, 1049–1051).—Invert sugar solution (1 per cent.), heated with lime water (0.5 per cent.) at 66.5° , gives a white, voluminous, flocculent precipitate which probably consists of basic calcium glucate; it dissolves when further

heated, becomes dark brown on exposure to air, and is sparingly soluble in water. The precipitate cannot be removed by filtration; it was washed six times with lime water by decantation, treated with dilute sulphuric acid, and extracted with ether; this extract, when evaporated, left a syrup, together with needle-shaped crystals, probably consisting of glucic acid; after remaining for some time in a desiccator, the needles disappeared, and crystals resembling those of cane sugar were produced (apoglucic acid?); finally, these dissolved, the syrup darkened, gas was evolved, and a black resin was formed which yielded carbonic anhydride and formic acid when distilled with steam. The acid could not be recrystallised.

J. B. T.

New Synthesis of Uric acid and of its Methyl Derivatives.

By EMIL FISCHER and LORENZ ACH (*Ber.*, 1895, **28**, 2473—2480; compare Liebig and Wöhler, *Annalen*, **24**, 284; Schlieper and Baeyer, *Annalen*, **127**, 3; Horbaczewski, *Abstr.*, 1885, 1050; 1887, 918; Behrend and Roosen, *Abstr.*, 1887, 581).—When Schlieper and Baeyer's pseudo-uric acid is fused with a large excess of oxalic acid at a temperature of 145—185° for 10 minutes, it loses a molecule of water, and yields uric acid. The dimethylpseudouric acid of Tschow (*Abstr.*, 1895, i, 84), when treated in a similar manner, yields a dimethyluric acid, which melts at 370°; it is moderately soluble in hot water, sparingly in cold water, in alcohol, and in acetone, but readily dissolves in ammonia, forming an *ammonium salt*, which can be obtained in a crystalline form by concentrating the solution. The *silver salt* is a gelatinous precipitate, which decomposes slowly at ordinary temperatures, but much more readily when warmed.

Another compound, which is formed in small quantity by the action of oxalic acid on dimethylpseudouric acid is E. Fischer and Reese's deoxyamalic acid (*Abstr.*, 1884, 466); this forms a sparingly soluble sodium salt, and readily yields murexoin when treated with bromine and then with ammonia. If dimethylpseudouric acid is added to a mixture of acetic anhydride and zinc chloride, a yield of 25 per cent. of γ -dimethyluric acid is obtained. When the lead salt of this acid is heated, at 120°, with methylic iodide and ether, a new β -trimethyluric acid is formed. This β -acid melts between 315° and 320°, at the same time undergoing decomposition; it is readily soluble in dilute alkalis, moderately in hot alcohol, and only sparingly in cold water and in alcohol. It gives the murexide reaction, is not readily acted on by phosphorus pentachloride, and, when heated with concentrated hydrochloric acid at 150°, yields carbonic anhydride, methylamine, and glycocine. When the lead salt of β -trimethyluric acid is further methylated, it yields the same tetramethyluric acid as is obtained from the α -trimethyl acid.

J. J. S.

Formation of Methyluric Acids from Theobromine.

By EMIL FISCHER (*Ber.*, 1895, **28**, 2480—2495).—When bromotheobromine is heated with normal potassium hydroxide solution for eight

hours on the water bath, the chief product is *δ*-dimethyluric acid, $\text{NMe}\cdot\text{CO}\cdot\text{C}\cdot\text{NMe}$
 $\begin{array}{c} \text{CO}-\text{NH}\cdot\text{C}-\text{NH} \\ | \quad | \end{array} > \text{CO}$, accompanied by a small quantity of a bromine derivative, which can be removed by reduction with hydriodic acid. The acid is decomposed at a higher temperature, when it evolves unpleasant smelling gases; it is only sparingly soluble in cold water, and crystallises from boiling water in prismatic plates, and readily gives the murexide reaction. The *ammonium*, *sodium*, and *potassium salts* are readily soluble in water, the *silver salt* forms a colourless, amorphous powder soluble in ammonia. When the lead salt is treated with methylic iodide and ether at 165–170°, it yields the trimethyluric acid previously described by the author (Abstr., 1884, 1309), to which the formula $\text{NMe}\cdot\text{CO}\cdot\text{C}\cdot\text{NMe}$
 $\begin{array}{c} \text{CO}-\text{NH}\cdot\text{C}-\text{NH} \\ | \quad | \end{array} > \text{CO}$ is given.

Chlorocaffeine, when heated with alcoholic potash, readily yields ethoxycaffeine; aqueous potash reacts in a more complicated manner, and even with very dilute alkali only a small quantity of hydroxycaffeine is formed. Bromoxanthine is very stable, and the greater part remains unaltered, even when heated for six hours at 135–140° with normal potassium hydroxide.

Chlorodioxydimethylpurin, $\text{C}_7\text{H}_7\text{N}_4\text{O}_2\text{Cl}$, is obtained when *δ*-dimethyluric acid (1·5 parts) is heated with phosphorus pentachloride (2 parts) and oxychloride (4 parts) at 140–145°. It forms small, colourless needles, and melts at 290° (corr.), at the same time undergoing decomposition. When reduced with hydriodic acid and phosphonium iodide, it gives *β*-dioxydimethylpurin, which is entirely decomposed at 370°; this is readily soluble in dilute alkalis and mineral acids, gives an amorphous silver salt, an *aurochloride* which crystallises in fine, yellow needles, and also a yellow *platinochloride*. The base, in contradistinction to the xanthine bases, does not give the murexide reaction.

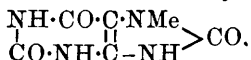
β-Trichloromethylpurin, is the final product of the action of phosphorus pentachloride on *δ*-dimethyluric acid, on theobromine or on caffeine, the yield is much better when chlorodioxydimethylpurin is first formed, and this is then treated with an excess of phosphorus pentachloride. It is readily soluble in hot alcohol and in benzene, sparingly in hot water, crystallises in fine, colourless needles, melts at 159–161° (corr.), and may be distilled in small quantities.

β-Dichloroxymethylpurin, $\text{N}:\text{CCl}\cdot\text{C}\cdot\text{NMe}$
 $\begin{array}{c} \text{CCl}\cdot\text{N}\cdot\text{C}-\text{NH} \\ | \quad | \end{array} > \text{CO}$, is formed when *β*-trichloromethylpurin is boiled with 40 times its weight of 20 per cent. hydrochloric acid for 10–15 minutes. It crystallises in small, colourless needles, melts and evolves gas at 278° (corr.), and is readily soluble in hot acetone but only sparingly in chloroform. It has acid properties, readily dissolves in cold alkalis, and yields a *silver derivative* which crystallises in slender needles; when the silver or lead salt is methylated, it yields dichloroxydimethylpurin (Abstr., 1884, 996).

β-Oxymethylpurin, $\text{C}_6\text{H}_6\text{N}_4\text{O}$, is obtained by the reduction of *β*-dichloroxymethylpurin with hydriodic acid and phosphonium

iodide; it crystallises in fine, colourless needles, melts at 266—267° (corr.), and is readily soluble in hot water, but only sparingly in cold. It forms salts with both acids and alkalis, the *platinochloride* forms large, yellow crystals, and the *aurochloride*, $C_6H_5N_4O, HAuCl_4$, large, yellow plates.

When heated at 130° with hydrochloric acid (sp. gr. 1.19), trichloromethylpurin is converted into γ -methyluric acid,



This acid crystallises with $1H_2O$, which it loses at 140°, decomposes at 370—380° without melting, and readily gives the murexide test. The *sodium* and *ammonium* salts are readily soluble in water, the *silver salt* is obtained quite colourless on the addition of a small quantity of silver nitrate to a solution of the ammonium salt; if too much silver nitrate is used, the salt becomes black. When heated with fuming hydrochloric acid at 170°, it is decomposed into carbonic anhydride, ammonia, and sarcosine; and when oxidised with potassium chlorate and hydrochloric acid, it yields alloxan and monomethylurea.

When trimethyluric acid is treated with phosphorus pentachloride and oxychloride at 130—150°, the dichloroxydimethylpurin previously described is formed.

J. J. S.

Action of Sulphurous Acid on Potassium Cyanide: Diazo-methanedisulphonic acid. By HANS VON PECHMANN and PHILIPP MANCK (*Ber.*, 1895, **28**, 2374—2383; compare *ibid.*, Ref., 522).—*Hydrogen potassium amidomethanedisulphonate*, $HSO_3 \cdot CH(NH_2) \cdot SO_3K$, is obtained by dissolving 100 grams of 99 per cent. potassium cyanide in a solution of hydrogen potassium sulphite, prepared by saturating a solution of 150 grams of caustic potash in 600 grams of water with sulphurous anhydride; the acid liquid is heated on the water bath, and becomes alkaline after 30—40 minutes. The solution is then carefully acidified with hydrochloric acid, and again warmed, addition of acid being repeated until the acidity is permanent, this being usually the case after $1\frac{1}{2}$ —2 hours. On adding concentrated hydrochloric acid to the cold liquid, about 200—250 grams of the hydrogen potassium salt crystallises out. It is a snowy powder, which dissolves but sparingly in water, yielding an acid solution; boiling water resolves it into the components.

Dipotassium amidomethanedisulphonate is prepared by allowing the mixed solution of potassium cyanide and hydrogen potassium sulphite to remain for several days at the ordinary temperature without previous treatment with acid; it crystallises from the liquid in rhombohedra, or in nodules of slender needles. It is more conveniently prepared by neutralising a solution of the foregoing salt with potassium carbonate. Recrystallised from hot water rendered feebly alkaline, it contains $1H_2O$, which is removed at 105°; it dissolves very readily in water, undergoing decomposition when the solution is boiled, yielding the components. Formic acid, ammonia, potassium thiosulphate, and potassium thiocyanate are also produced,

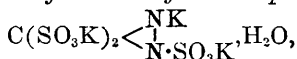
the two last-named being secondary products due to the action of potassium sulphite on formic acid and of potassium thiosulphate on potassium cyanide respectively.

Dipotassium diazomethanedisulphonate, $C(SO_3K)_2 < \overset{N}{\underset{N}{\parallel}} H_2O$, is prepared in the following manner. Hydrogen potassium amidomethanedisulphonate (23 grams) is mixed with water (34 grams) and treated with a 66 per cent. solution of potassium nitrite (15 grams) at 15–16°; as the salt passes into solution, the temperature gradually rises to 40–45°, and, after 10–15 minutes, the orange-yellow liquid, which effervesces slightly, is rendered alkaline with caustic potash, and allowed to cool. The salt, recrystallised from 2 parts of boiling water containing a small quantity of potash, is obtained in orange-yellow needles or prisms containing $1H_2O$, which is removed in a vacuum at 60–90°. At higher temperatures, water and sulphurous anhydride are liberated, the salt becoming colourless; in dealing with a small quantity, this change occurs at 210°, and the residue consists of potassium sulphate, thiosulphate, and formate. The salt is readily soluble in water, forming a neutral solution which gradually becomes acid and evolves gas, energetic liberation of nitrogen taking place in the boiling liquid; this gas is evolved quantitatively on treating the salt with acids.

Dipotassium iodomethanedisulphonate, $CHI(SO_3K)_2 \cdot 2H_2O$, is prepared by adding 30 per cent. hydriodic acid (12 grams) to a solution of the diazo-salt (10 grams) in water (100 grams); after 10 hours, the solution is treated with alcohol, and the precipitate thus obtained redissolved in a small quantity of warm water to which acetone is then added, the salt being obtained in aggregates of long needles. It contains $2H_2O$ which is eliminated at 105°; the boiling solution yields silver iodide when treated with silver nitrate.

Dipotassium diodomethanedisulphonate, $CI_2(SO_3K)_2$, is obtained by adding iodine (15 grams) in small quantities to a solution of the diazo-salt (20 grams in 120 grams of water), mixed with a solution of potassium hydrogen carbonate (22 grams in 88 grams of water); it crystallises from boiling water in lustrous, rectangular leaflets, and becomes yellow when exposed to light. Silver nitrate precipitates silver iodide from the boiling solution, but no change is produced in solutions of this or the foregoing salt by salts of other metals. Sodium amalgam converts both iodomethanedisulphonates into dipotassium methanedisulphonate.

Basic potassium sulphohydrazimethylenedisulphonate,



is obtained by gently heating the diazo-salt (30 parts) with a solution of potassium sulphite, prepared by neutralising with potassium carbonate (9–10 parts) a solution of hydrogen potassium sulphite (45 parts), formed by saturating a solution of caustic potash (1 : 5) with sulphurous anhydride. It is very soluble in water, forming an alkaline solution which yields a precipitate with barium chloride; this is dissolved by hydrochloric acid, and on heating the liquid,

barium sulphate is thrown down, this being due to the quantitative elimination of the sulphonic group attached to nitrogen. When the salt is decomposed with sulphuric acid, hydrazine sulphate is formed, carbonic and sulphurous anhydrides being eliminated (compare Abstr., 1895, i, 647).

The normal salt, $C(SO_3K)_2 \cdot \begin{smallmatrix} NH \\ | \\ N \cdot SO_3K \end{smallmatrix} \cdot 1\frac{1}{2}H_2O$, crystallises in small, lustrous prisms from a concentrated solution of the basic salt which has been saturated with glacial acetic acid. It is readily soluble in water, and the solution gives no precipitate with barium chloride.

Hydroxymethanetrissulphonic acid, $C(SO_3H)_3 \cdot OH$, is obtained, in the form of its potassium salt, when the hydrazine-compound or the diazo-salt is treated with boiling water; the yield is more satisfactory when the latter is heated with a solution of hydrogen potassium sulphite. The potassium salt is identical with the compound described by Albrecht (*Annalen*, 1872, **161**, 139). The barium salt crystallises in lustrous leaflets, and contains $4H_2O$. M. O. F.

Chloro-derivatives of α -Dithienyl. By OTTO EBERHARD (*Ber.*, 1895, **28**, 2385—2386).—Monochlorodithienyl, obtained by the action of concentrated sulphuric acid on monochlorothiophen (Abstr., 1894, i, 117) is converted by excess of sulphuryl chloride into *tetrachloro- α -dithienyl*, $C_8H_2Cl_4S_2$; this crystallises in small, yellowish-brown needles, melting at 126.5 — 127° (corr.). When it is heated with two molecular proportions of sulphuryl chloride at 200° , it yields *perchlorodithienyl*, $C_8Cl_6S_2$, which forms long, reddish-yellow needles, melting at 211.5 — 212.5° (corr.). *Tetrachlorodithienyl* is converted by bromine into *tetrachlorodibromodithienyl*, $C_8Br_2Cl_2S_2$, which crystallises in hard yellowish needles, and melts at 189.5 — 190° (corr.). All these products can also be prepared from the synthetical α -dithienyl, and this fact proves that the dithienyl derivatives previously described by the author belong to the same series. A. H.

Synthesis of Aromatic Hydrocarbons. By ALBERT TÖHL (*Ber.*, 1895, **28**, 2459—2463; compare Abstr., 1891, 1022; Töhl and Geyger, Abstr., 1892, 968; Töhl and Karchowski, Abstr., 1892, 990, and Jannasch and Wigner, Abstr., 1895, i, 655). In preparing propyltoluene by Fittig's method of synthesis, the author observed that propylic bromide gave a much better yield than the iodide. The author in conjunction with Tripke now shows that a fairly good yield of propylmesitylene may be obtained by the action of propylic bromide on mesitylic iodide, or still better on mesitylic bromide in the presence of sodium and ether. Ethylmesitylene has been obtained in a similar manner, but the yield is not so good as that obtained by Jannasch when working with a xylene solution. Cymene has also been synthesised in a similar manner by the action of sodium on isopropylic bromide and parabromotoluene.

Propylmesitylene boils at 220 — 221° , does not solidify at -20° , has a sp. gr. = 0.8773 at 20° , and when oxidised yields mesitylenecarboxylic acid (Jannasch and Weiler, Abstr., 1895, i, 283).

Dibromopropylmesitylene crystallises from alcohol in slender, long needles and melts at 56° .

Barium propylmesitylenesulphonate, $(C_{12}H_{17}SO_3)_2Ba + 2H_2O$, crystallises from water in small, glistening plates. The *sodium salt*, $C_{12}H_{17}SO_3Na + 2H_2O$, is readily soluble in water. The *calcium salt* crystallises with $1H_2O$, and the *magnesium salt* with $2H_2O$, but the *copper salt* is anhydrous. *Propylmesitylenesulphonamide* crystallises from concentrated solutions in small needles, which melt at $98-99^{\circ}$.

Dinitropropylmesitylene, obtained by dissolving the hydrocarbon in cold, fuming nitric acid, crystallises in small colourless needles, and melts at $93-94^{\circ}$. A substance, which melts at 135° , is also formed, but the constitution of this product has not yet been determined.

Nitropropylmesitylene, obtained by slowly dropping double the theoretical quantity of fuming nitric acid into the hydrocarbon, is an oily product, and on reduction yields *amidopropylmesitylene*, which is also an oil. The amido-compound yields a *sulphate*, which is readily soluble in water, crystallises in small needles and melts at 117° , and an *acetyl* derivative which melts at 161° .

Ethylmesitylene boils at $207-209^{\circ}$ (uncorr.) whereas Jannasch gives $212-214^{\circ}$ as the boiling point. *Dibromethylmesitylene*, $C_6Br_2Me_3Et$, melts at 219° , and the *dinitro-derivative*, $C_6Me_3Et(NO_2)_2$, at 123° . The *sulphonic acid* yields a *barium salt* which is very readily soluble in water, and also a *sodium salt*, $C_{11}H_{15}SO_3Na + H_2O$, which loses its water of crystallisation when kept over sulphuric acid.

J. J. S.

Action of the Monobromo-derivatives of the Aromatic Hydrocarbons on the Lead Salts of the Thiophenols. By ED. BOURGEOIS (*Ber.*, 1895, **28**, 2312-2330).—When an aromatic monobromo-derivative is heated with the lead salt of an aromatic thiophenol, the latter dissolves at a temperature which is usually below 175° . When the solution is heated, action takes place in two stages; in the first between 180° and 190° , $2(RS)_2Pb + 4R'Br = (RS)_2Pb, PbBr_2 + RSR' + 2R'Br$, the double compound of the lead salt and lead bromide separate in the solid form, at a higher temperature, $225-230^{\circ}$, the reaction is completed in accordance with the equation $(RS)_2Pb, PbBr_2 + 2R'Br = RSR' + 2PbBr_2$. The author proposes to measure the velocity of the reaction during the first stage, which is undisturbed by secondary actions, and thus to obtain some idea as to the effect of the nature of the aromatic group on the power of the bromine atom to enter into reaction. The following new sulphides have been obtained by the above method in the course of the preliminary experiments.

All the sulphides when pure have a faint and not unpleasant odour, but acquire the usual smell of garlic when distilled. *Phenylic metatolylic sulphide* boils at 309.5° , and has the sp. gr. 1.1058 at $0^{\circ}/4^{\circ}$. *Phenylic paratolylic sulphide* melts at 15.7° , boils at 311.5° , and has the sp. gr. 1.09 at its melting point. *as-Phenylic orthoxylylic sulphide*, $(Me_2 : S = 1 : 2 : 4)$, boils at 181.5° (pressure = 11 mm.) and has the sp. gr. 1.0962 at $0^{\circ}/4^{\circ}$. *as-Phenylic metaxylylic sulphide*, $[Me_2 : S = 1 : 3 : 4]$,

boils at 172.5° (pressure = 11 mm.) and has the sp. gr. 1.0935 at $0^{\circ}/4^{\circ}$. *Phenylic paraxylylic sulphide* [$\text{Me}_2 : \text{S} = 1 : 4 : 2$] boils at 171° (pressure = 11 mm.) and has the sp. gr. 1.0913 at $0^{\circ}/4^{\circ}$. *Phenylic mesitylic sulphide* boils at 180° (pressure = 11 mm.) and has the sp. gr. 1.0817 at $0^{\circ}/4^{\circ}$. *Orthoparaditolyl sulphide* boils at 173° (pressure = 11 mm.) and has the sp. gr. 1.0889 at $0^{\circ}/4^{\circ}$. *Metaparaditolyl sulphide* crystallises in lustrous needles, melts at 27.8° , and boils at 179° (pressure = 11 mm.). *Paratolylic orthoxylylic sulphide* [$\text{Me}_2 : \text{S} = 1 : 2 : 4$] forms crystalline granules melting at 28.6° . It boils at 193.7° (pressure = 11 mm.). *Paratolylic metaxylylic sulphide* [$\text{Me}_2 : \text{S} = 1 : 3 : 4$] boils at 188° (pressure = 11 mm.) and has the sp. gr. 1.0716 at $0^{\circ}/4^{\circ}$. *Paratolylic paraxylylic sulphide*, [$\text{Me}_2 : \text{S} = 1 : 4 : 2$] melts at 6° and boils at 185° (pressure = 11 mm.). The liquid has the sp. gr. 1.072 at $0^{\circ}/4^{\circ}$. *Paratolylic mesitylic sulphide* crystallises in small, lustrous needles, melts at 89.6° , and boils at 190° (pressure = 11 mm.). *Orthoxylylic α -naphthyl sulphide* is a yellow liquid which boils at 246° (pressure = 11 mm.), and has the sp. gr. 1.1346 at $15^{\circ}/4^{\circ}$. *Orthoxylylic β -naphthyl sulphide* melts at 68° and boils at 251.5° (pressure = 11 mm.). *Metaxylylic α -naphthyl sulphide* is a yellowish liquid, which boils at 239.5° (pressure = 11 mm.) and has the sp. gr. 1.1355 at $15^{\circ}/4^{\circ}$. *Metaxylylic β -naphthyl sulphide* crystallises in lustrous needles, melts at 39.6° and boils at 243.5° (pressure = 11 mm.). *Paraxylylic α -naphthyl sulphide* forms needles, melts at 36.2° and boils at 235° (pressure = 11 mm.). *Paraxylylic β -naphthyl sulphide* also forms needles, melts at 36.7° and boils at 240° (pressure = 11 mm.). *Mesitylic α -naphthyl sulphide* crystallises in large, lustrous tablets, melts at 120.6° and boils at 245° (pressure = 11 mm.). *Mesitylic β -naphthyl sulphide* crystallises in prisms melting at 87.5° , and boils at 245° (pressure = 11 mm.). The temperatures given are corrected. A. H.

Potassium Derivatives of Quinone and Quinol. By CHARLES ASTRE (*Compt. rend.*, 1895, **121**, 326—328).—When an ethereal solution of quinone is boiled with potassium, hydrogen is liberated, and the compound $\text{C}_6\text{H}_3\text{KO}(\text{OH}) + \text{Et}_2\text{O}$ is obtained as a deep green compound, which oxidises very rapidly when exposed to air, and becomes incandescent when heated at 100° or brought in contact with a mineral acid. In presence of benzene, the action of potassium on quinone yields quinhydrone and a brownish-green crystalline compound which oxidises with great rapidity, becomes incandescent in moist air, and takes fire if rubbed in presence of air. In contact with water, it is converted into a blue compound, which rapidly becomes brown; in contact with inorganic acids, it becomes incandescent. It seems to have the composition $\text{C}_{12}\text{H}_7\text{O}_4\text{K}_3$.

The action of potassium on quinol in presence of ether, yields a white, crystalline compound, $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{OK} \cdot \text{C}_6\text{H}_4(\text{OH})_2$, which rapidly oxidises, and becomes first blue, then greyish-white, and finally very dark brown, in presence of moist air or oxygen.

The formation of these compounds supports the view that quinone is a diketone.

C. H. B.

Action of Sodium Alkylxides on Chloranil. Acetals derived from Substituted Quinones. By C. LORING JACKSON and H. S. GRINDLEY (*Amer. Chem. J.*, 1895, **17**, 579—607).—*Dichlorodiphenoxyquinone*, $C_6Cl_2O_2(OPh)_2$, is prepared by heating chloranil (25 grams) with an aqueous solution of phenol (25 grams) and potassium hydroxide (12 grams) on the water bath, and recrystallising the separated solid from benzene. It crystallises in aggregates of red needles, melts at 243° , and dissolves sparingly in alcohol, benzene, and chloroform, freely in hot glacial acetic acid, and not at all in water, ether, light petroleum, carbon bisulphide, or acetone. Caustic soda hydrolyses it, forming chloranilic acid. It is not reduced by sulphurous acid at 100° , but hydriodic acid converts it into *dichlorodiphenoxyquinol*. $C_6Cl_2(OH)_2(OPh)_2$, which crystallises in large colourless prisms and in arborescent needles, melts at 197 — 198° , and dissolves in most solvents except water, benzene, and light petroleum.

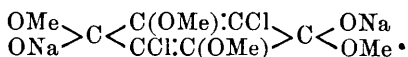
When warmed with aniline, dichlorodiphenoxyquinone yields dichlorodianilidoquinone.

Tetrethyllic dichloroquinonedimalonate, $C_6Cl_2O_2[CH(COOEt)_2]_2$, is prepared by mixing dichlorodiphenoxyquinone with alcohol and ethylic sodiomalonate, when a dark blue precipitate separates; this is washed with alcohol, dissolved in water, and the solution treated with acid. The new compound crystallises in long, slender, stellate needles, melts at 132° , and dissolves in alcohol, but not in water. By reduction, it yields the corresponding quinol, already described by Stieglitz (*Abstr.*, 1891, 455). As already indicated, the *sodio*-derivative $C_6Cl_2O_2[CNa(COOEt)_2]_2$, has a blue colour, and is soluble in water, but not in alcohol. When the quinone is boiled with sodium carbonate in absolute alcohol, *tetrethyllic diethoxyquinonedimalonate*, $C_6O_2(OEt)_2[CH(COOEt)_2]_2$, is obtained; this forms nearly white crystals, melts at 115° , and dissolves in alcohol and ether, but not in water.

Dichlorodimethoxyquinone dimethylhemiacetal, $C_6Cl_2(OH)_2(OMe)_2$, is prepared by warming dichlorodiphenoxyquinone (10 grams) with a methylic alcohol solution of sodium (2.5 grams) methoxide; the white crystalline compound which separates, is dissolved in water and treated with dilute sulphuric acid, when the new compound is precipitated. The same compound is formed when chloranil is treated with a solution of sodium methoxide in methylic alcohol. It is a white, amorphous solid, insoluble in all common solvents, and is easily converted into dichlorodimethoxyquinone (methylic chloranilate, *Abstr.*, 1890, 136) either by heat or by dilute acids; it is a feeble acid, forming a white crystalline compound with sodium methoxide. *Dichlorodiethoxyquinone diethylhemiacetal*, $C_6Cl_2(OH)_2(OEt)_2$, is similarly prepared, sodium ethoxide and ethylic alcohol being substituted for the methoxide and methylic alcohol respectively; it is a white, amorphous solid, which dissolves slightly in alcohol, but is partially decomposed thereby; it is insoluble in all other common solvents. At 140 — 143° it is converted into dichlorodiethoxyquinone (*loc. cit.*), and melts; dilute acids effect the same change. *Dichlorodimethoxyquinone diethylhemiacetal*, $C_6Cl_2(OMe)_2(OH)_2(OEt)_2$, was prepared from dichlorodi-

methoxyquinone and sodium ethoxide in alcoholic solution; it is similar in properties to the two preceding compounds.

The authors discuss the constitution of these hemiacetals in some detail. They find them to be incapable of reduction to quinols or of forming oximes with hydroxylamine hydrochloride, so that the ketonic character of the parent quinones has been lost; from this it is concluded that the sodium salt of dichlorodimethoxyquinone dimethylhemiacetal, for instance, has the constitution



It is suggested that the constitution of phenoquinone and quinhydrone is similar to that of these hemiacetals. A. G. B.

Hydrolysis and Synthesis of Dihydroresorcinol. By DANIEL VORLÄNDER (*Ber.*, 1895, **28**, 2348—2349; compare *Abstr.*, 1894, **i**, 528).—It has been already shown (*loc. cit.*) that phenyldihydroresorcinol is converted into phenylacetylbutyric acid when treated with hydrolytic agents. The author finds that dihydroresorcinol behaves in the same way on subjection to similar treatment, yielding γ -acetylbutyric acid when heated with a concentrated solution of barium hydroxide during several hours at 150—160°; the semicarbazone dissolves with difficulty in water, and crystallises in lustrous leaflets melting at 164—166°.

The reaction by which dihydroresorcinol is converted into γ -acetylbutyric acid is reversible, dihydroresorcinol being produced when ethylic γ -acetylbutyrate is treated with sodium ethoxide; this is the simplest case of passing between the aromatic and aliphatic series.

Dihydroresorcinol is not formed by the action of ethylic sodacetate on ethylic acrylate, the product being ethylic α -acetylglutamate. M. O. F.

Action of Bromine on Anethoöl. By CARL HELL and O. VON GÜNTHERT (*J. pr. Chem.*, 1895, [2], **52**, 193—210; compare *Abstr.*, 1895, **i**, 341).—In the preparation of bromanethoöl dibromide, the use of hot alcohol must be avoided, since, when hot, this solvent reacts with the dibromide, removing 1 mol. HBr, and forming a compound which crystallises in long prisms and melts at 62°. A study of the behaviour of the dibromide with hot water led to no definite conclusion.

When bromanethoöl dibromide is dissolved in aniline, aniline hydrobromide separates, and the filtrate from this yields a yellow powder, $\text{C}_{16}\text{H}_{16}\text{OBrN}$ (m. p. 75°), when decomposed by hydrochloric acid; this compound yields bromanisic acid when oxidised with potassium permanganate. The dibromo-ketone obtained by oxidising bromanethoöl dibromide (*Abstr.*, 1895, **i**, 341) also yields an aniline derivative, $\text{C}_{16}\text{H}_{16}\text{O}_2\text{BrN}$, when heated with aniline; this crystallises in small aggregates of needles, melts at 119°, and dissolves easily in ether, alcohol, benzene, and chloroform, but only sparingly in light petroleum; it dissolves in strong sulphuric acid, and is precipitated unchanged therefrom by water; the compound appears to have been

formed by the substitution of the aniline residue for the bromine atom of the side chain.

Anethoïl dibromide also yields a *ketone*, $C_{10}H_{11}BrO_2$, when oxidised with chromic acid in an acetic acid solution (compare *loc. cit.*); this forms large, strongly refractive crystals, melts at $65-67^\circ$, and dissolves in alcohol, ether, and light petroleum; the compound has a pungent odour, and burns the skin. When heated with alcoholic ammonia on the water bath, the ketone dissolves, and the solution leaves, when evaporated, a *compound*, which is probably an isoindole-like compound of the form $N \leq \begin{smallmatrix} CMe \\ | \\ CH(C_6H_4 \cdot OMe) \end{smallmatrix}$; this is a yellow,

crystalline powder, melts at 176° , and dissolves easily in ether, but only sparingly in alcohol, and not at all in light petroleum. Oxidation with potassium permanganate converts the ketone into anisic acid.

Two *dibromanethoïl dibromides*, $C_{10}H_{10}Br_4O$, were obtained by heating bromanethoïl dibromide with bromine (1 mol.) in a sealed tube; the one crystallises when the ethereal solution of the product of the action is evaporated, and forms slender needles which melt at $113-114^\circ$; the other remains as a syrup when the ether has been evaporated, and crystallises from this after a time; it melts at 89° , and is much more soluble in light petroleum than its isomeride. Reduction with zinc dust converts the dibromide into dibromanethoïl. The dibromide reacts with aniline to form the *compound* $C_{10}H_{10}OBr_2N$, which melts at 82° . Oxidation with chromic acid in acetic acid solution, converts the dibromide into a *ketone*, $C_{10}H_9Br_2O_2$, which contains two nucleal bromine atoms; it is a yellow powder, melts at 135° , and dissolves easily in ether, benzene, and chloroform. Two acids were extracted by sodium carbonate from the crude product of the oxidation of the dibromide; one of these melts at 85° , and is also formed when the ketone is oxidised by potassium permanganate; but neither has been identified. The *compound* $C_{10}H_9Br_2NO$, which is obtained by the action of alcoholic ammonia at 180° on the ketone, is insoluble in most organic solvents, and sublimes, without melting, at a high temperature. The behaviour of the ketone with aniline is also described.

A. G. B.

The Cholesterols of Cryptogams. By ERNEST GÉRARD (*J. Pharm.*, 1895, [6], 1, 601—608; compare *Abstr.*, 1892, 1294).—The author has extracted cholesterol from ordinary brewer's yeast, from a common mould (*Mucor mucedo*), and from a lichen (*Lobaria pulmonacea*). The processes adopted in the three cases were similar.

Yeast (30 kilos.) containing 25—30 per cent. of solid matter is extracted with a large quantity of 96 per cent. alcohol. The residue, dried at $40-50^\circ$, and the aqueous solution left on distilling off the alcohol, are extracted with ether, and the combined ethereal extracts, which contain the cholesterol, together with the fatty matter and other substances, are evaporated to dryness; the cholesterol and fats are then extracted from this residue with light petroleum, and, after the removal of the solvent, are boiled with alcoholic potash to liberate the cholesterol. The alcohol having been removed, the cholesterol is extracted with ether from the aqueous alkaline soap solution, and

the crystals thus obtained are washed with alcohol, and recrystallised from ether or benzene.

The cholesterol of yeast crystallises in rectangular plates or slender needles melting at $135-136^{\circ}$, and has a specific rotatory power, $[\alpha]_D = -105^{\circ}$. No analysis is given. It is very sparingly soluble, even in boiling alcohol, but readily in the usual organic solvents. The benzoate could not be prepared in a pure state.

The mould was cultivated in a 6 per cent. solution of milk sugar containing the usual inorganic salts. Owing to the comparatively small amount of material available, the amount of cholesterol obtained was very minute, but it crystallised in plates, and appeared from its reactions to be identical with Tanret's ergosterine.

The product obtained from the lichen also crystallised in needles and plates, and exhibited similar reactions.

The cholesterol from cryptogams differs from animal cholesterol in its colour reactions with sulphuric acid. The latter gives a yellowish colour with the concentrated acid, which blackens on the addition of water, whilst under the same conditions the former gives a red colour, changing to blue. Similar colorations are yielded by carbon tetrachloride solutions of the cholesterol, with the exception that the yellow solution turns white instead of black; the chloroform solutions also exhibit analogous colour changes. JN. W.

Electrolytic Reduction of Paranitro-compounds dissolved in Sulphuric acid. By ARTHUR A. NOYES and JOHN J. DORRANCE (*Ber.*, 1895, 28, 2349—2352; compare *Abstr.*, 1893, i, 406; also 1894, i, 503).—A large platinum electrode is fitted closely to the side of a small beaker, in which is placed a porous cylinder containing a small platinum electrode; 20—30 grams of the nitro-compound is dissolved in two to three times its weight of concentrated sulphuric acid, and transferred to the beaker, whilst the porous cell, originally filled with concentrated sulphuric acid, is replenished from time to time with dilute acid. A current of 1 or 2 ampères is employed during 40—50 hours.

Paranitraniline yields paradiamidobenzene sulphate, paranitrophenol giving rise to paramidophenolsulphonic acid, which is also formed when parachloronitrobenzene is reduced.

The paper contains a short summary of the results hitherto obtained. M. O. F.

Action of Aniline on Mercurous Iodide. By MAURICE FRANÇOIS (*Compt. rend.*, 1895, 121, 253—256).—When mercurous iodide is mixed with excess of aniline in the cold, metallic mercury separates, and diphenyldimercurammonium iodide, $HgI_2 \cdot 2NH_2Ph$, is formed and dissolves. At the boiling point of the aniline, the change takes place very rapidly. With aniline in smaller proportion, but still in excess, some of the mercurous iodide remains unchanged, and if mercuric iodide is dissolved in its own weight of warm aniline, and mercury is added, a small quantity of mercurous iodide forms on the surface of the metal. It follows that the action is, to a certain extent, reversible, and the author finds that when equilibrium is established at the boiling point of aniline, there are 26.35 parts of mercuric iodide

in every 100 parts of the solution. The result is the same, whether the original substances are aniline and mercurous iodide, or aniline, mercuric iodide, and mercury. The quantity of mercuric iodide in solution when equilibrium is established varies with the temperature, but an exact determination was only made at the boiling point of the aniline.

A solution of mercuric iodide in aniline containing 26 parts of the salt in 100 parts of solution, does not decompose mercurous iodide at 182° , but dissolves it in considerable quantity, and the mercurous salt separates in crystals when the liquid is cooled, whilst the undissolved mercurous iodide, if the latter is in excess, is also found to have become crystalline.

C. H. B.

Halogen Additive Products of the Anilides. By HENRY L. WHEELER (*Amer. Chem. J.*, 1895, **17**, 612—619).—*Metanitracetanilide dibromide*, $C_8H_8N_2O_3Br_2$, is prepared by acting on metanitracetanilide in nitrobenzene with bromine, washing with light petroleum, and crystallising from chloroform. It forms stellate, yellow prisms, and melts and effervesces at 143° . Water removes hydrogen bromide from it, yielding *parabromometanitracetanilide*, which crystallises in yellow needles, and melts at 143° .

Bromonitraniline, $[NH_2:NO_2:Br = 1:3:4]$, is obtained when parabromometanitracetanilide is boiled with alcohol and strong hydrochloric acid. It crystallises in slender, yellow needles, and melts at 131° . Its *hydrochloride* and *sulphate* are described.

The author shows that in the above dibromide the bromine atoms are probably attached to the benzene nucleus, not to the nitrogen of the anilide group.

A. G. B.

Behaviour of Ethers of Azophenol on Reduction with Stannous Chloride and Hydrochloric acid. By PAUL JACOBSON (*Annalen*, 1895, **287**, 97—147; compare Abstr., 1893, i, 327; and 1894, i, 26).—The paper forms an introduction to the matter brought forward in the following abstracts; it is divided into three portions, dealing respectively with the results of the investigation, their theoretical bearing, and the methods which have been adopted in the course of the work.

The changes involved when ethers of azophenol are reduced, follow three alternative courses, resulting in the formation of orthosemidine bases, parasemidine bases, and scission bases, the quantity in which bases of each class is produced being influenced by the nature of the azophenol derivative employed, and by the position in the molecule occupied by the substituent. The author has, therefore, collected in a table the quantitative results obtained on reducing various derivatives of benzeneazophenetoil.

M. O. F.

Reduction of Benzeneazo-orthocresetoil and Benzeneazo-metacresetoil. By PAUL JACOBSON, F. K. FERTSCH, FRED. MARSDEN, and G. SCHKOLNIK (*Annalen*, 1895, **287**, 147—160).—Benzeneazo-orthocresetoil yields the orthosemidine base, 2:4:5-*amidoethoxy*-

methyldiphenylamine, $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{Me}(\text{OEt})\cdot\text{NHPh}$, which crystallises in lustrous leaflets, and melts at $94-95^\circ$; the *hydrochloride* is crystalline. The *azimide*, $\text{C}_{15}\text{H}_{15}\text{N}_3\text{O}$, is obtained by the action of nitrous acid on the base, and crystallises in colourless needles melting at 118° ; the *methenyl* derivative, $\text{C}_{16}\text{H}_{16}\text{N}_2\text{O}$, formed on treating the base with boiling formic acid, crystallises from petroleum, and melts at 102° , whilst the *nitrate* and *hydrochloride* crystallise in needles. The *thiocarbenyl-compound*, $\text{C}_{16}\text{H}_{16}\text{N}_2\text{OS}$, is obtained by heating the base with carbon bisulphide and alcohol; it crystallises in small needles, softens at 225° , and melts at $238-240^\circ$. The *stilbazonium base*, $\text{C}_{23}\text{H}_{28}\text{N}_2\text{O}_2$, is obtained by condensation with benzile; it forms lustrous, lemon-yellow leaflets, and melts at 136° . *Monanilidotoluquinone* is obtained by oxidising the orthosemidine base with ferric chloride, and is also formed in preparing the azimide by treatment with nitrous acid; it crystallises from alcohol in lustrous, violet-red needles, and melts at 148° . *Dianilidotoluquinone* is produced when the foregoing substance is treated with aniline in alcoholic solution; it separates from glacial acetic acid in the form of a crystalline powder, and does not melt below 300° .

The orthosemidine base is not the sole product of reduction of benzeneazo-orthocresetol, a small quantity of a parasemidine base, 4-amido-4':3'-ethoxymethyldiphenylamine, $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{OEt}$, which crystallises from petroleum in lustrous, colourless needles, and melts at $110-111^\circ$ being obtained; the *acetyl* derivative crystallises in rosettes of needles, and melts at 173° . From 10 grams of benzeneazo-orthocresetol, 4.95 grams of the orthosemidine base were obtained, the yield of the parasemidine base amounting to 2.1 grams, whilst 2 grams of scission bases were also formed.

Benzeneazometacresetol, $\text{OEt}\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{N}_2\text{Ph}$, crystallises in orange-red needles, and melts at 51.5° ; the chief product of its reduction is the parasemidine base, 4-amido-4':2'-ethoxymethyldiphenylamine, which crystallises from petroleum in pink prisms, and melts at 61° . The *monacetyl* derivative of this base melts at $97-98^\circ$; the *diacetyl* derivative at 153° . The *thiocarbamide* crystallises in nacreous leaflets, and melts at 181.5° . 4.7 grams of the parasemidine base were obtained from 10 grams of benzeneazometacresetol, 4.1 grams of mixed aniline and metacresetidine being formed at the same time.

M. O. F.

Reduction of Ethers of Tolueneazophenols. By PAUL JACOBSON, FR. DÜSTERBEHN, J. KLEIN, and G. SCHKOLNIK (*Annalen*, 1895, **287**, 161—183).—Reduction of orthotolueneazophenetoil gives rise to the parasemidine base 4:3:4'-amidomethylethoxydiphenylamine (D. R. P., 75,292), which crystallises from petroleum in colourless needles, and melts at 82° ; the *hydrochloride* dissolves in cold water with extreme difficulty, and crystallises in leaflets. The *diazoidide* is formed when a solution of the diazo-chloride is poured into aqueous potassium iodide, and crystallises in reddish-yellow needles. The *monacetyl* derivative melts at 156° , and the *diacetyl* derivative at $180-181^\circ$; the *benzylidene* derivative and *orthohydroxybenzylidene* derivative melt at $86-87^\circ$ and $124-125^\circ$ respectively. 4:4':3-Chlor-

ethoxymethyldiphenylamine is obtained from the parasemidine base by Sandmeyer's reaction, and melts at 77—78°; the *nitrosamine* melts at 49—50°. From 10 grams of orthotolueneazophenetoil, 5.1 grams of the parasemidine base were formed, 3.6 grams of a mixture of orthotoluidine and phenetidine being formed at the same time.

Metatolueneazophenetoil, $C_6H_4Me \cdot N_2 \cdot C_6H_4 \cdot OEt$, crystallises from alcohol in orange-red prisms, and melts at 65°; on reduction, it yields approximately equal quantities (26—28 per cent.) of orthosemidine and parasemidine bases. The *hydrochloride* of the former, 2 : 5 : 3'-*amidoethoxymethyldiphenylamine*, was isolated, but the base has not been obtained in the crystalline state; the *azimide* forms colourless needles, and melts at 110—111°, and the *stilbazonium base* crystallises in lustrous, yellow needles, and melts at 176°. The *methenyl* compound was obtained in the form of the *nitrate*, which crystallises in needles. The parasemidine base, 4 : 4' : 2-*amidoethoxymethyldiphenylamine*, crystallises in long, colourless needles, which rapidly become blue when exposed to air, and melts at 92—93°; the *hydrochloride* crystallises from hot water in colourless leaflets, and the *monacetyl* derivative melts at 112—113°. An attempt has been made to obtain this base by synthetical means. 4' : 2-*Ethoxymethyldiphenylamine* was prepared by the action of ethylic bromide and sodium ethoxide on hydroxymethyldiphenylamine; it separates from petroleum in pale yellow crystals, and melts at 81—82°, boiling under atmospheric pressure at 354° (uncorr.). The *nitrosamine* melts at 71—72°, but the transformation of this derivative into the parasemidine base has not been effected in a satisfactory manner.

Reduction of paratolueneazophenetoil, which is first converted into paratoluenehydrazophenetoil, gives rise to an orthosemidine base, which is either 2 : 5 : 4'-*amidoethoxymethyldiphenylamine*, or 2 : 4' : 5-*amidoethoxymethyldiphenylamine*, in quantity amounting to 18 per cent., a mixture of paratoluidine and paraphenetidine being also produced to the extent of 69 per cent. Neither the *hydrochloride* nor the base has been analysed; the *azimide*, however, crystallises in colourless leaflets, and melts at 117—118°, and the *stilbazonium base* crystallises from alcohol in yellow needles, sinters at 141°, and melts at 144—146°.

When the isobutyl ether of paratolueneazophenol is reduced, 72 per cent. of the material employed, is obtained as a mixture of paratoluidine and the isobutyl ether of paramidophenol, the products of the semidine transformation not having been, in this case, examined. The benzyl ether of paratolueneazophenol yields paratoluidine and *paramidophenyl benzylic ether*, which crystallises in silky leaflets, and melts at 56° (Abstr., 1893, i, 330); the *acetyl* derivative melts at 139°. The mixture of these bases amounts to 78.5 per cent. of the material employed.

M. O. F.

Reduction of Tolueneazocresetoils. By PAUL JACOBSON, E. HEBER, F. HENRICH, and C. SCHWARZ (*Annalen*, 1895, **287**, 183—211).—Orthotolueneazo-orthocresetoil crystallises in red, transparent aggregates, and melts at 35—37°; the difficulty with which it solidifies accounts for the observation of Noelting and Werner (Abstr.,

1891, 214), who describe this substance as a red oil. On reduction, it yields the orthosemidine base, 2 : 5-*amidoethoxy*-2' : 4-*dimethyldiphenylamine*, which crystallises in flat prisms, and melts at 78°; the *hydrochloride* is an oil which rapidly solidifies. The *thiocarbenyl-compound*, $C_{17}H_{18}N_2OS$, melts at 253°, and the *stilbazonium base* crystallises from alcohol in small, yellow needles, and melts at 153°. Oxidation with ferric chloride converts the orthosemidine base into *orthotoluidotoluquinone*, which crystallises in dark, lustrous leaflets, and melts at 145—146°. The parasemidine base, 4 : 4' : 3 : 3'-*amidoethoxydimethyldiphenylamine*, is also formed on the reduction of orthotoluene-orthocresetoil; it crystallises in colourless leaflets, becomes red when exposed to air, and melts at 86°. The *monacetyl* derivative melts at 143°, the *thiocarbamide* at 179—180°, and the *diformyl* derivative at 146—147°. The ortho- and para-semidine bases are obtained in quantities amounting to 29 and 36 per cent. respectively, the remainder of the product consisting of scission bases.

Metatolueneazo-orthocresol, $C_6H_4Me \cdot N_2 \cdot C_6H_3Me \cdot OH$ [N : Me : OH = 1 : 3 : 4], is obtained by bringing together diazotoluene chloride and orthocresol in molecular proportion; it crystallises from benzene in lustrous, golden yellow needles, and melts at 115°. *Metatolueneazo-orthocresetoil* crystallises in reddish-yellow plates, and melts at 46—47°. When this ether is reduced, the orthosemidine base, 2 : 5-*amidoethoxy*-3' : 4-*dimethyldiphenylamine*, is produced in quantity amounting to 43 per cent. of the material employed; it crystallises from petroleum in aggregates of colourless needles, and melts at 91—91.5°. The *azimide* crystallises from petroleum in leaflets, and melts at 83—84°; the *stilbazonium base* melts 137.5—140°, and the solution in alcohol exhibits greenish-yellow fluorescence. Oxidation with ferric chloride converts the orthosemidine base into *metatoluidotoluquinone*, which forms purple-red needles, and melts at 142°. The parasemidine base, 4 : 4' : 2 : 3'-*amidoethoxydimethyldiphenylamine*, is also formed when metatolueneazo-orthocresetoil is reduced, the yield amounting to rather more than 5 per cent. It crystallises from petroleum in long needles, and melts at 99—100°.

Reduction of paratolueneazo-orthocresetoil gives rise to the orthosemidine base, 2 : 5 : 4 : 4'-*amidoethoxydimethyldiphenylamine*, which crystallises from dilute alcohol in small, white needles, which become violet when exposed to light or air, and melt at 76°. The *azimide* crystallises in colourless leaflets, and melts at 131°, the *thiocarbenyl-compound* at 205—206°, and the *stilbazonium base* at 146—149°. The yield of the orthosemidine base amounts to 50 per cent., 21 per cent. of mixed bases being also obtained.

Orthotolueneazometacresol crystallises in orange-red plates, and melts at 112°; the *sodium* derivative crystallises in lustrous, yellow leaflets. *Metacresolbisazo-orthotoluene*, $(C_6H_4Me \cdot N_2)_2C_6H_2Me \cdot OH$, is formed during the preparation of the phenol, and melts at 188°. *Orthotolueneazometacresetoil* crystallises from alcohol in deep red, lustrous needles, and melts at 64°; when this substance is reduced 43 per cent. of the parasemidine base, 4 : 4' : 3 : 2'-*amidoethoxydimethyldiphenylamine*, is formed, 53 per cent. of other bases being produced at the same time. The base crystallises in white leaflets,

and melts at 86° ; the *sulphate* crystallises from alcohol in long, colourless needles, and the *monacetyl* derivative and *diacetyl* derivative melt at 144° and 115° respectively.

Metatolueneazometacresol crystallises in orange-yellow, rhombic plates, and melts at 106 – 107° ; during its preparation *metacresolbisazometatoluene* is formed, crystallising in long, reddish-brown needles, and melting at 102 – 103° . *Metatolueneazometacresetol* crystallises from alcohol in red prisms, and melts at 73° ; on reduction, it yields 44 per cent. of the parasemidine base, $4:4':2:2'$ -amidoethoxydimethyldiphenylamine, which crystallises in colourless prisms from benzene to which petroleum has been added; it melts at 95 – 96° , the *monacetyl* derivative at 116° , and the *thiocarbamide* at 70 – 72° .

Paratolueneazometacresol crystallises from benzene in orange-red prisms, and melts at 135° ; *metacresolbisazoparatoluene* is formed at the same time, and melts at 107° . *Paratolueneazometacresetol* crystallises from alcohol in orange-red, four-sided plates, and melts at 64° ; on reduction, it yields 24 per cent. of an orthosemidine base. The *stilbazonium* base crystallises in long, canary-yellow needles, and melts 178 – 179° .
M. O. F.

Reduction of Metaxyleneazophenetoil. By PAUL JACOBSON and G. SCHKOLNIK (*Annalen*, 1895, **287**, 211–212).—*Metaxyleneazophenol* crystallises from benzene in brown prisms, and melts at 134° . *Metaxyleneazophenetoil* crystallises in red needles, and melts at 97° . On reducing this substance, 74 per cent. of mixed bases is obtained, consisting of xylidine and phenetidine.
M. O. F.

Reduction of Azophenetoils. By PAUL JACOBSON and FRIEDRICH MEYER (*Annalen*, 1895, **287**, 212–220).—*Orthophenetoilazoparaphenol*, $\text{OEt}\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{C}_6\text{H}_4\cdot\text{OH}$, is obtained by adding a solution of diazotised phenetidine to a well-cooled solution of sodium phenoxide containing 1 gram of phenol to 25 grams of water; it crystallises from benzene in lustrous, reddish-brown leaflets, and melts at 131° . *Orthophenetoilazoparaphenetoil* crystallises from alcohol in brown leaflets with a golden lustre, and melts at 77 – 78° . When this substance is reduced, the parasemidine base, $4:3:4'$ -amidodiethoxydiphenylamine, is obtained; this crystallises from petroleum in lustrous, feathery leaflets, and melts at 84.5° ; the *hydrochloride* forms aggregates of colourless needles, which rapidly become blue. The *thiocarbamide* melts at 154.5 – 155° . The parasemidine base is obtained in quantity amounting to 51 per cent. of the material employed.

Metaphenetoilazoparaphenol melts at 105 – 106° , *metaphenetoilparaphenetoil* at 70 – 71° ; on reduction, the latter yields 69 per cent. of a mixture consisting of ortho- and para-semidine bases.

Paraphenetoilazoparaphenol melts at 125 – 126° , and not at 104.5° as already stated (D. R. P., 48,543). On reducing the ethyl ether, 95 per cent. of paraphenetidine was obtained.
M. O. F.

Constitution of the Hydroxyazo-compounds. By WILLIAM MCPHERSON (*Ber.*, 1895, **28**, 2414–2418).—Two views have been held with regard to the constitution of the hydroxyazo-compounds;

one that their constitution is that denoted by the name, the other that they are in reality quinone-derivatives. Benzoquinone reacts with phenylhydrazine and its alkyl derivatives to form quinol, free nitrogen, and other products. With β -benzoylphenylhydrazine, however, it reacts like a ketone, *quinonemonophenylbenzoylhydrazone*,



being formed. This substance crystallises in yellowish needles, or in groups of flat prisms, which melt at 171° . It is quantitatively converted by zinc dust and acetic acid into benzanilide and paramidophenol; this reaction is exactly similar to that shown by many of the acetic and benzoic derivatives of the orthohydroxyazo-compounds.

Quinonebenzoylhydrazone explodes when it is brought in contact with phenylhydrazine, and even in alcoholic solution a vigorous action, accompanied by evolution of nitrogen, takes place. Quinonebenzoylhydrazone, which from its properties and the method by which it is obtained, must have the formula given above, is entirely different in its properties from the benzoate of parahydroxyazobenzene (*Ber.*, **6**, 561), which is hydrolysed by concentrated sulphuric acid or alcoholic potash into benzoic acid and parahydroxyazobenzene, and therefore appears to have the formula $\text{OBz}\cdot\text{C}_6\text{H}_4\cdot\text{N}\cdot\text{NPh}$. This true hydroxyazo-compound is converted by zinc dust and acetic acid into a dihydrogen derivative, which is probably the corresponding hydrazo-compound.

Quinonebenzoylhydrazone, like the benzoate of parahydroxyazobenzene, is converted by sulphuric acid or alcoholic potash into benzoic acid and parahydroxyazobenzene, so that the two isomeric benzoic derivatives yield, on hydrolysis, only one compound (compare *Nef, Annalen*, **287**, 354).

These results seem to show that parahydroxyazobenzene really has the constitution indicated by its name, and is a true hydroxy-derivative and not a quinone derivative. The research is being extended to the naphthalene derivatives. A. H.

Rules controlling the Formation of Azo-colouring Matters.

By WILHELM VAUBEL (*J. pr. Chem.*, 1895, [2], **52**, 284—288).—The author points out that the formation of azo-colouring matters may be well compared with the bromination of aromatic hydroxy- and amido-compounds. Such differences as are noticeable may be traced to the closer relationship of the amido-group to the azo-group than to the hydroxyl-group, and to the smaller acidifying power of the azo-group as compared with that of the bromine atom, as well as in the spacial relationship of the azo-group towards the bromine atom. It must further be noted that bromination takes place in acid solution, whilst the formation of azo-dyes is generally effected in alkaline or neutral solutions, seldom in the presence of acids. A. G. B.

Symmetrical Dibenzylhydrazine (Hydraziphenylmethane).

By THEODOR CURTIUS and E. QUEDENFELDT (*Ber.*, 1895, **28**, 2345—2347; compare *Abstr.*, 1889, 393).—*Symmetrical dibenzylhydrazine*, $\text{CH}_2\text{Ph}\cdot\text{NH}\cdot\text{NH}\cdot\text{CH}_2\text{Ph}$, is obtained by reducing benzylideneazine in

alcoholic solution with sodium amalgam; it crystallises in large, lustrous plates, and melts at 65° . On remaining exposed to the atmosphere, it becomes converted into a colourless oil. The base is indifferent towards alcohol, water, acids, and alkalis, and does not reduce Fehling's solution; it reduces a cold, ammoniacal silver solution however. The *monohydrochloride* is not decomposed on exposure to air; it crystallises in colourless prisms, and melts at 153° . The *picrate* is insoluble in water, but crystallises from alcohol in long, golden-yellow prisms, and melts at 130° . The *acetyl* derivative crystallises in colourless needles, and melts at 78° ; the *benzoyl* derivative melts at 87° , and the *nitroso*-derivative, which crystallises from alcohol in large, yellow prisms, at 89° . When the nitroso-derivative is treated with reducing agents, ammonia is formed, together with dibenzylhydrazine or benzylamine, according as reduction is mild or energetic.

Oxidation of dibenzylhydrazine in alcoholic solution with mercuric oxide, leads to the formation of a *compound* which crystallises from alcohol in colourless prisms, and melts at 152° ; although having the empirical formula of azobenzyl, its molecular weight is found to be twice as great, and it probably has the constitution

$$\begin{array}{c} \text{CH}_2\text{Ph}\cdot\text{N}\cdot\text{N}\cdot\text{CH}_2\text{Ph} \\ \text{CH}_2\text{Ph}\cdot\text{N}\cdot\text{N}\cdot\text{CH}_2\text{Ph} \end{array}$$

Benzylideneazine tetrabromide, $\text{CHBrPh}\cdot\text{NBr}\cdot\text{NBr}\cdot\text{CHBrPh}$, is obtained by adding bromine to a chloroform solution of benzylideneazine; it forms orange-red crystals, and melts at 134° . On dissolving it in acetone, a colourless liquid is obtained, bromacetone and the *dihydrobromide* of benzylideneazine being formed. Liberation of nitrogen takes place when benzylideneazine tetrabromide is dissolved in alcohol; the reaction proceeds quantitatively, mineral acids and boiling water producing the same effect.

M. O. F.

Tautomerism. By WILLY MARCKWALD (*Annalen*, 1895, 286, 343—368; compare *Abstr.*, 1895, i, 347).—The author is of opinion that the amidines are tautomeric compounds, and that the hypothesis of pseudomerism cannot be applied to them. Derivatives of this class would be expected to behave consistently with having both the structures $\text{NHR}'\cdot\text{CR}\cdot\text{NR}''$ and $\text{NR}'\cdot\text{CR}\cdot\text{NHR}''$; this is actually the case, and where contradictions have occurred in the apparent existence of two isomerides, repetition of the experiments in question has established their inaccuracy. The author criticises von Pechmann's views regarding the constitution of formazyl-compounds (*Abstr.*, 1894, i, 456), and discusses the subject of tautomerism at some length.

In the formulæ given below it is to be understood that the tautomeric formula is also implied in each case.

Orthoparaditolylacetamidine, $\text{C}_6\text{H}_4\text{Me}\cdot\text{N}\cdot\text{CMe}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\text{Me}$, is obtained from ethylisothioacetorthotoluidide and paratoluidine, or from ethylisothioacetoparatoluidide and orthotoluidine (Wallach and Wüsten, *Ber.*, 1883, 16, 148). It crystallises from alcohol in needles, and melts at 144 — 145° ; the same product is obtained from both sources, and the previous investigators were mistaken in recognising two modifications.

Phenylparatolylbenzamidine (von Pechmann, Abstr., 1895, i, 347) is obtained from benzanilide imidochloride and paratoluidine, or from benzoparatoluidide imidochloride and aniline; the two forms originally described by von Pechmann are identical, as he, himself, has since shown (*loc. cit.*), and both preparations, when recrystallised, melt at 131—132° to a turbid liquid, which becomes clear at 133°. The *nitrate* forms small, white crystals, and melts and decomposes at 144°; the *hydrochloride* melts at 237°, and the *picrate* at 195°.

Diphenylparatolylguanidine, $C_6H_4Me \cdot N:C(NHPh)_2$, is formed from aniline and phenyltolylcyanamide; aniline, phenyltolylthiocarbamide, and lead oxide; paratoluidine, diphenylthiocarbamide, and lead oxide, or from paratoluidine and diphenylcyanamide; Huhn, by means of the first two methods, obtained products which he believed to be different from one another (Abstr., 1886, 1036). The base separates from alcohol in white crystals, and melts at 128—129°; the *hydrochloride* melts at 221—222°, and the *platinochloride* becomes brown at 230°, but does not melt at this temperature.

Tetraphenylparatolylidiguanide,



is obtained as a bye-product in preparing the foregoing compound from diphenylcyanamide and paratoluidine; it crystallises from absolute alcohol, and melts at 150°. It is prepared by allowing the latter substance to remain in alcoholic solution with the former (2 mols.) for one day. The *hydrochloride* melts and decomposes at 156°, and the *platinochloride* melts at 136°.

Pentaphenyldiguanide, $NHPh \cdot C(NPh) \cdot NPh \cdot C(NPh) \cdot NHPh$, is a bye-product in the preparation of triphenylguanidine; it is also prepared by allowing an alcoholic solution of aniline and diphenylcyanamide to remain for one day at the ordinary temperature. It melts at 160°, and when heated with aniline yields triphenylguanidine. The *hydrochloride* melts at 213°, and the *platinochloride* is amorphous.

Phenyldiorthotolylguanidine, $NPh:C(NH \cdot C_6H_4Me)_2$, was described by Huhn, who obtained a product melting at 102° from diorthotolylcyanamide and aniline, and from diorthotolylthiocarbamide, aniline, and lead oxide, whilst a preparation from phenylorthotolylcyanamide and orthotoluidine, or from phenylorthotolylthiocarbamide and orthotoluidine by the action of lead oxide, melted at 112°. Making use of these four methods, the author has been able to isolate one form only of phenyldiorthotolylguanidine; this separates from alcohol in well-formed, colourless crystals, and melts at 97—98°; the *hydrochloride* melts at 197°, and the *nitrate* melts and decomposes at 183°; the *platinochloride* forms minute orange-yellow crystals, and melts at 213—214°. When the base is prepared by either of the methods indicated, tritolylguanidine (m. p. 130—131°) is formed at the same time; its *hydrochloride* melts above 250°, and the *nitrate* decomposes and melts at 204°. The action of carbon bisulphide on phenyldiorthotolylguanidine affords evidence of the tautomeric nature of this substance; if its structure is to be represented by the tautomeric formulæ $NPh:C(NH \cdot C_6H_4Me) \cdot NH \cdot C_6H_4Me$ and



a mixture of diorthotolylthiocarbamide and phenylthiocarbimide with phenylorthotolylthiocarbamide and orthotolylthiocarbimide should be formed under the influence of carbon bisulphide, whilst a substance having a rigid structure would yield only one thiocarbamide and one thiocarbimide. Experiment shows that the former alternative takes place, irrespective of the source from which the base is derived.

Diphenylorthotolylguanidine, $C_6H_4Me \cdot N : C(NHPh)_2$, is the sole product of the action of orthotoluidine on diphenylcyanamide; it separates from alcohol in white crystals, and melts at 112° . The *nitrate* melts at 172° , and the *platinochloride* at 210° .

Tetraorthotolylphenyldiguamide,



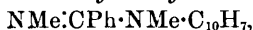
is obtained by the union of aniline with diorthotolylcyanamide (2 mols.); it crystallises from alcohol in white needles, and melts at 111° . The *hydrochloride* and the *platinochloride* are sparingly soluble in water. M. O. F.

Mixed Amidines and Tautomerism. By HANS VON PECHMANN (*Ber.*, 1895, 28, 2362—2374; compare *Abstr.*, 1895, i, 347).—Former experiments have dealt with the tautomerism of the types $NX \cdot R \cdot NHY$ and $NHX \cdot R \cdot NY$, in which X and Y represent chemically similar radicles; in the present series, the radicles are dissimilar, and it is found in consequence that tautomerism does not occur.

Methylbenzamide imidochloride, $CPhCl \cdot NMe$, is obtained by the action of phosphorus pentachloride on methylbenzamide; it is a colourless, mobile liquid which has an irritating odour, and boils at 124° under a pressure of 60 mm., undergoing slight decomposition.

β -*Naphthylamidobenzenylmethylimidine*, $NMe \cdot CPh \cdot NH \cdot C_{10}H_7$, is obtained by allowing β -naphthylamine to act on the foregoing substance dissolved in ether, or from β -benzonaphthalide imidochloride and methylamine. It separates from much boiling alcohol in lustrous crystals, and melts at 204° . The crystalline form is monosymmetric, $a : b : c = 1.8456 : 1 : 0.70848$; $\beta = 81.39^\circ$. The *picrate* crystallises in sulphur-yellow prisms, and melts at 166.5° .

β -*Naphthylmethylamidobenzenylmethylimidine*,



is obtained by methylating the foregoing substance, and is identical with the amidine obtained from methylbenzamide imidochloride and β -methylnaphthylamine; it is an oil which readily forms the *picrate*, crystallising in orange-yellow plates, melting at 155.5° .

Dimethylamidobenzenyl- β -naphthylimidine. $Me_2N \cdot CPh \cdot NC_{10}H_7$, is formed when dimethylamine remains in contact with benzonaphthalide imidochloride; the *hydriodide* crystallises from ether in colourless prisms, and melts at 215° , whilst the *picrate* forms bright yellow prisms, and melts at 150° .

Phenylamidobenzenylmethylimidine, $MeN : CPh \cdot NHPh$, is obtained by the action of aniline on methylbenzamide imidochloride, and of methylamine on benzanilide imidochloride; it crystallises from alcohol in colourless needles, and melts at 134° . The *picrate* melts at 169° , and the *hydriodide* at 190° .

Methylphenylamidobenzenylmethylimidine, $\text{MeN}:\text{CPh}:\text{NMePh}$, is produced on methylating the foregoing substance; it crystallises from petroleum, and melts at 56° . The *hydriodide* is colourless, and melts at 190° ; the *picrate* melts at 174° .

Dimethylamidobenzenylphenylimidine, $\text{Me}_2\text{N}:\text{CPh}:\text{NPh}$, is obtained from benzanilide imidochloride and dimethylamine; it melts at $73\text{--}74^\circ$. The *hydriodide* forms lustrous prisms, and melts at 196° ; the *picrate* melts at 126° .

Phenylamidobenzenylanilimidine, $\text{NHPh}:\text{CPh}:\text{N}:\text{NHPh}$, is obtained by heating a mixture of benzanilide imidochloride and phenylhydrazine on the water bath; it crystallises in yellow prisms, and melts at 119° . Ferric chloride develops a red coloration in the alcoholic solution; in concentrated sulphuric acid, the same coloration is developed by potassium dichromate, whilst ferric chloride produces no change. Fehling's solution is slowly reduced on boiling. The *hydrochloride* is sparingly soluble, and crystallises in needles, and the *picrate* melts and decomposes at 202° .

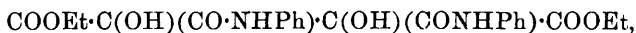
Anilamidobenzenylphenylimidine, $\text{PhN}:\text{CPh}:\text{NH}:\text{NHPh}$, is produced by heating a solution of benzophenylhydrazide imidochloride in benzene with aniline, and also in the preparation of the foregoing base; it crystallises in lustrous needles, and melts at $174\text{--}175^\circ$. Ferric chloride develops a brown coloration in the alcoholic solution, and a violet coloration in concentrated sulphuric acid solution; Fehling's solution is reduced on boiling. The *hydrochloride* is readily soluble, and crystallises in needles; the *picrate* melts and decomposes at 175° .
M. O. F.

Action of Phenyl isocyanate on some Acids and Ethereal Salts. By ALBIN HALLER (*Compt. rend.*, 1895, 121, 189—193).—Phenyl isocyanate and cyanacetic acid, in molecular proportion, react at the ordinary temperature, and yield *cyanacetanilide*, $\text{CN}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NHPh}$, which crystallises from alcohol in nacreous white plates melting at 199° . Methylsalicylic acid and phenyl isocyanate at 120° yield *methylsalicylanilide*, which melts at 62° , and is not affected by water or by boiling aqueous potash. Anisic acid, on the other hand, at 120° , yields anisic anhydride, identical with that obtained by the action of phosphorus oxychloride on sodium anisate; at $180\text{--}190^\circ$, however, it yields anisanilide. Anisic acid, therefore, behaves in the same manner as benzoic, toluic, phthalic, camphoric, and other acids (*Abstr.*, 1895, i, 679). Phenylglycollic acid yields only phenylglycollamide, $\text{OH}\cdot\text{CHPh}\cdot\text{CO}\cdot\text{NHPh}$, melting at $145\text{--}146^\circ$.

Benzoylbenzoic acid and phenyl isocyanate, in presence of ether or light petroleum, yield unstable crystals, which readily split up into their proximate constituents when dissolved in any hot neutral solvent. If, however, the two compounds are heated at 100° in the absence of any solvent, symmetrical diphenylcarbamide and benzoylbenzoic acid are formed; the latter crystallises from alcohol in transparent, lozenge-shaped crystals melting at $140\text{--}141^\circ$, and is identical with the anhydride obtained by von Pechmann by heating

acetylbenzoylbenzoic anhydride at 200° , this product melting at $140-141^{\circ}$, and not at 120° , as stated by Pechmann.

At $140-150^{\circ}$, benzoylbenzoic acid and phenylic isocyanate seem to yield benzoylbenzanilide, but the latter could not be isolated. It follows that benzoylbenzoic acid behaves both as a lactone-alcohol, $\text{CO} < \text{C}_6\text{H}_4 > \text{CPh}\cdot\text{OH}$, and as an acid ketone, $\text{COOH}\cdot\text{C}_6\text{H}_4\cdot\text{COPh}$. Ethylic tartrate and phenylic isocyanate, in presence of dry benzene, at 130° yield the compound



which crystallises from benzene in white needles melting at 164° , and, when dissolved in chloroform, has a molecular rotatory power $[\alpha]_{\text{D}} = -61\cdot56^{\circ}$.
C. H. B.

Action of Benzoic Chloride on Urethane. By HANS VON PECHMANN and LUDWIG VANINO (*Ber.*, 1895, **28**, 2383—2384).—Benzoylurethane is obtained by heating a mixture of urethane, benzoic chloride, and pyridine, in molecular proportion, for 10—12 hours in boiling water; the mass is agitated with caustic soda and ether, and the alkaline liquid acidified. A solution of the product in alcohol deposits *ethylic benzoylallophanate*, $\text{COPh}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}\cdot\text{COOEt}$, which crystallises in silky needles, and melts at 179° (compare Kretschmar, *Ber.*, 1875, **8**, 104), whilst benzoylurethane (m. p. 110°) crystallises from the mother liquor. When ethylic benzoylallophanate is heated above its melting point, it solidifies at $200-205^{\circ}$, phenylic cyanide distilling over; the residue crystallises from alcohol in lustrous leaflets, and melts at 223° .
M. O. F.

Syntheses with Sodamide Derivatives. By CARL BLACHER (*Ber.*, 1895, **28**, 2352—2360; compare *Abstr.*, 1895, i, 289).—The author has continued his study of sodamide derivatives, and included sodium succinimide and sodium phthalimide in the investigation.

Sodium succinimide yields benzylsuccinimide when heated with excess of benzylic chloride for four hours in a reflux apparatus; sodium acetanilide gives rise to acetobenzylanilide. Benzoic anhydride and acetic anhydride yield with sodium benzamide, dibenzamide and acetylbenzamide respectively; diacetanilide is formed when acetic anhydride acts on sodium acetanilide.

The action of sodium or potassium ethylic sulphate on sodium benzamide and sodium phthalimide leads to the formation of ethylbenzamide and ethylphthalimide respectively.
M. O. F.

Ethereal Imidocarbonates and the so-called Normal Ethereal Cyanates. By ARTHUR R. HANTZSCH and LUDWIG MAI (*Ber.*, 1895, **28**, 2466—2472).—The authors agree with Nef (*Annalen*, **287**, 310) in stating that the ethereal salts of cyanic acid described by Cloez (*Annalen*, **102**, 355) have no existence. The products of the reaction between cyanogen chloride and sodium alkylloxides consist mainly of the ethereal salts of imido-carbonic acid (as much as
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92 per cent.), together with small quantities of ethereal salts of cyanuric acid.

Phenylic imidocarbonate, NH:C(OPh)_2 , is most readily obtained by the action of cyanogen bromide (1 mol.) on a mixture of sodium phenoxide (1 mol.) and phenol (1 mol.), dissolved in ether. It forms a hard, white mass, melts at 54° , and readily undergoes decomposition even at the ordinary temperature, yielding phenylic cyanurate and phenol. The decomposition takes place much more rapidly when the solution of the phenylic imidocarbonate in light petroleum is heated for several hours.

By no alterations in the methods of procedure, were the authors enabled to obtain normal phenylic cyanate.

Parabromophenylic imidocarbonate, $\text{NH:C(O}\cdot\text{C}_6\text{H}_4\text{Br)}_2$, is readily obtained by the action of parabromophenol (2 mols.) on cyanogen bromide (1 mol.); it melts at 129° , is sparingly soluble in ether and cold alcohol, and is also more stable than the corresponding phenylic salt.

Ethylic imidocarbonate is very stable, and is only decomposed into alcohol and ethylic cyanurate when heated in sealed tubes at 200° for several hours. Aqueous solutions of the imido-ether, when treated with an alkaline solution of bromine, give a precipitate of *ethylic bromimidocarbonate*, NBr:C(OEt)_2 ; this is readily soluble in ether, and crystallises in needles, which melt at 43° .

No trace of ethylic cyanate could be obtained by the action of cyanogen bromide on sodium ethoxide, nor yet of methylic cyanate from sodium methoxide. The chief product was always the imido-ether, together with small quantities of the cyanurate.

Sodium phenoxide and also sodium parabromophenoxide cause the condensation of phenylic isocyanate into phenylic isocyanurate. The polymeride of phenylic isocyanate obtained by Hofmann (*Annalen*, **1**, 57) differs from this cyanurate, and is shown to be a dimolecular isocyanate, whereas the isocyanurate is a tri-molecular compound.

J. J. S.

Benzazide (Benzoylazoimide). Acid Azides of the Fatty Series. By THEODOR CURTIUS (*J. pr. Chem.*, 1895, [2], **52**, 210—226; compare Abstr., 1895, i, 32).—Benzoylazoimide (benzazide) (Abstr., 1891, 56) is best purified by dissolving it in acetone, from which it crystallises in large, colourless tables melting at 32° . Its behaviour with water, with alcohol, with bromine, and with aniline has been described (Abstr., 1894, i, 331; 1895, i, 32). Dimetanitrodiphenylcarbamide melts at $247\text{--}250^\circ$, not at 233° as heretofore stated.

When reduced by means of sodium amalgam in alcohol, benzoylazoimide is converted into ethylic benzoate and sodium azoimide; when alcoholic ammonium sulphide is the reducing agent, benzamide and ammonium azoimide are the products, hydrogen sulphide being liberated. When zinc dust and glacial acetic acid are used, benzamide can alone be isolated; but when caustic soda is substituted for acetic acid, sodium benzoate and sodium azoimide are formed, unless the solution is very dilute, when nitrogen is evolved and dibenzoylhydrazine (m. p. 233°), $\text{NHBz}\cdot\text{NHBz}$, produced (compare *loc. cit.*).

Phenylazoimide, PhN_3 , can be similarly reduced to hydrazobenzene, $\text{NHPh}\cdot\text{NHPh}$, by sodium amalgam in alcohol.

Succinylazoimide, $\text{C}_2\text{H}_4(\text{CO}\cdot\text{N}_3)_2$, is prepared by gradually adding sodium nitrite (2 mols.) to a well cooled, concentrated aqueous solution of succinylhydrazine hydrochloride (Abstr., 1895, i, 264), and shaking with ether. It crystallises in long prisms, and explodes when heated. It is easily soluble in alcohol, sparingly so in ether, and insoluble in water. Under water, it melts at 30° . Boiling water decomposes it with evolution of carbonic anhydride and nitrogen, and formation of ethylenecarbamide. Boiling alcohol decomposes it, with formation of ethylenediurethane (m. p. 110°).

Attempts to prepare oxalylazoimide, $\text{N}_3\cdot\text{CO}\cdot\text{CO}\cdot\text{N}_3$, have not been successful; treatment of oxalylhydrazide (*loc. cit.*) in the manner described in the preceding paragraph, yielded *hydrazioxalyl*, $\text{CO}\cdot\text{NH}\cdot\text{NH}\cdot\text{CO}$
 $\text{CO}\cdot\text{NH}\cdot\text{NH}\cdot\text{CO}$, which is a white solid, insoluble in all solvents.

Malonylazoimide, $\text{CH}_2(\text{CO}\cdot\text{N}_3)_2$, prepared by diazotising malonylhydrazine (*loc. cit.*) in the manner described for succinylhydrazide, is an explosive oil which is converted into a yellow oil when heated with alcohol; the reactions of the yellow oil prove it to be methylenediurethane.

Glycolylazoimide, $\text{OH}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{N}_3$, is easily obtained by diazotising glycolylhydrazine (Abstr., 1895, i, 331) hydrochloride; it crystallises in double pyramids, and explodes feebly. Boiling alcohol converts it into the *urethane*, $\text{OH}\cdot\text{CH}_2\cdot\text{NH}\cdot\text{COOEt}$, which melts at 189° .

A. G. B.

Azides (Azoides) of Substituted Benzoic acids. By A. STRUVE and RUDOLF RADENHAUSEN (*J. pr. Chem.*, 1895, [2], 52, 227—242).—*Metanitrobenzoylazoimide*, $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{N}_3$, is prepared by dissolving metanitrobenzoylhydrazine in dilute nitric acid, and adding the calculated quantity of sodium nitrite. It crystallises in white laminae, melts at 68° , and dissolves easily in ether, benzene, alcohol, and glacial acetic acid, but not in water. It is also the main product of the action between diazobenzene sulphate and metanitrobenzoylhydrazine. When heated with much water, it is converted into dimetanitrodiphenylcarbamide melting at 234° (compare preceding abstract). *Tetranitrodiphenylcarbamide* crystallises in yellow needles. When metanitrobenzoylazoimide is boiled with alcohol, it yields *metanitrophenylurethane*, $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{COOEt}$, which crystallises in yellow needles, melts at 56° , and dissolves easily in alcohol and ether; strong hydrochloric acid at 120° decomposes it into carbonic anhydride, alcohol, and metanitriline.

Orthonitrobenzoylazoimide is similarly prepared; it crystallises in yellow prisms, melts at 36° , and dissolves freely in ether, chloroform, and benzene, but only sparingly in light petroleum.

Paranitrobenzoylazoimide crystallises in colourless laminae, melts at 69° , and resembles the meta-derivative in solubility. Hot water converts it into *diparanitrodiphenylcarbamide*, $\text{CO}(\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2)_2$, which crystallises in lemon-yellow needles, melts above 260° , and is insoluble in water; hydrochloric acid at 130° decomposes it with formation of

paranitraniline, but the change is more difficult to accomplish than in the case of the meta-derivative. Hot alcohol converts paranitrobenzoylazoimide into paranitrophenylurethane (Abstr., 1885, 149).

Orthobromobenzoylhydrazine, $C_6H_4Br \cdot CO \cdot NH \cdot NH_2$, from ethylic orthobromobenzoate and hydrazine hydrate, crystallises in colourless needles, melts at 153° , and is only sparingly soluble in water, but freely so in alcohol and hot benzene.

Metahydroxybenzoylhydrazine, $OH \cdot C_6H_3 \cdot CO \cdot NH \cdot NH_2$, from ethylic metahydroxybenzoate and hydrazine hydrate, forms white crystals, melts at 150° , and dissolves in water and alcohol, but not in ether, chloroform, or benzene. When its aqueous solution is shaken with benzaldehyde, *benzylidenemetahydroxybenzoylhydrazine*,



separates; it melts at 205° .

Metahydroxybenzoylazoimide, $OH \cdot O_6H_4 \cdot CO \cdot N_3$, prepared by diazotising the hydrazine, forms small, nearly colourless crystals, melts at 95° , and dissolves easily in alcohol, ether, and chloroform, but only sparingly in light petroleum; when heated with water, it yields *dimetahydroxydiphenylcarbamide*, $CO(NH \cdot C_6H_4 \cdot OH)_2$, which forms colourless crystals, and melts at 220° .

Parahydroxybenzoylhydrazine, prepared like the meta-derivative, crystallises in white laminae, melts at 260° , and dissolves in hot water and alcohol. The corresponding *benzylidene* derivative forms white crystals, and melts at 218° . *Parahydroxybenzoylazoimide* crystallises in white needles, melts at 132° , and dissolves in ether, alcohol, benzene, and chloroform, but not in water. When it is heated with alcohol, it yields a crystalline compound which melts at 105 – 110° , and is converted by hot water into *diparahydroxydiphenylcarbamide*; this crystallises in colourless needles, and decomposes, without melting, at 230° .

Orthohydroxybenzoylhydrazine, prepared from methylic salicylate and hydrazine hydrate, crystallises in colourless laminae, and melts at 145° . The corresponding *benzylidene* derivative forms small, colourless crystals, and melts at 230° . *Orthohydroxybenzoylazoimide* crystallises in large, colourless, rhombic plates, melts at 27° , and has a powerful, tear-exciting odour. *Diorthohydroxydiphenylcarbamide* crystallises in white needles, and melts at 125° .

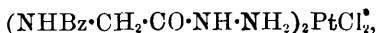
Metamidobenzoylhydrazine, $NH_2 \cdot C_6H_4 \cdot CO \cdot NH \cdot NH_2$, is prepared from ethylic metamidobenzoate and hydrazine hydrate. It forms colourless crystals, melts at 77° , and is very soluble in cold water and in alcohol; the *hydrochloride*, $NH_2 \cdot C_6H_4 \cdot CO \cdot N_2H_3 \cdot 2HCl$, melts at 265° . The *benzylidene* derivative, $NH_2 \cdot C_6H_4 \cdot CO \cdot NH \cdot N : CHPh$, melts at 180° . *Metamidobenzoylazoimide*, $NH_2 \cdot C_6H_4 \cdot CO \cdot N_3$, is precipitated by adding sodium acetate to a mixture of metamidobenzoylhydrazine and diazobenzene sulphate in aqueous solution; it crystallises in yellow needles, melts at 85° , and dissolves in ether, benzene, and light petroleum.

A. G. B.

Hydrazide and Azoimide of Hippuric Acid. By THEODOR CURTIUS (*J. pr. Chem.*, 1895, [2], 52, 243–271).—The author describes in detail the preparation of hippurylhydrazine (Abstr.,

1891, 56; 1892, 112; 1895, 32) by the action of hydrazine hydrate on (1) ethylic hippurate, (2) hippuramide, (3) hippurylazoimide, (4) ethylic hippurylglycolate.

Hippurylhydrazine hydrochloride, $\text{NHBz}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{NH}_2\cdot\text{HCl}$, forms colourless crystals. The *platinosochloride*,



crystallises in slender needles. Hippurylbenzylidenehydrazone has previously been described (Abstr., 1891, 56). *Hippurylcinnamylidenehydrazine*, $\text{NHBz}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{N}:\text{CH}\cdot\text{CH}:\text{CHPh}$, crystallises in yellowish prisms, and melts at $201\cdot5^\circ$. *Symmetrical acetylhippurylhydrazine*, $\text{NHBz}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{NHAc}$, is formed by the interaction of acetylhydrazine (Abstr., 1895, 263) with hippurylazoimide in ethereal solution; it crystallises in colourless needles, melts at 186° , and dissolves easily in alcohol. *Symmetrical hippurylphenylhydrazine*, $\text{NHBz}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{NHPh}$, from phenylhydrazine and hippurylazoimide, crystallises in silvery laminæ or needles, melts at $182\cdot5^\circ$, and can be distilled nearly undecomposed when quickly heated; it dissolves in hot alcohol, but not in water or in ether; it does not reduce hot Fehling's solution. *Nitrosohippurylphenylhydrazine*, $\text{NHBz}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{NPh}\cdot\text{NO}$, prepared by treating the last-named compound in glacial acetic acid solution with sodium nitrite, forms a yellow, crystalline powder, melts at $128\text{--}129^\circ$, and dissolves in alcohol, but not in water; hot water decomposes it into phenylazoimide and hippuric acid. *Acetylhippurylphenylhydrazine*,



prepared by digesting hippurylphenylhydrazine with acetic anhydride, forms a white, crystalline powder, melts at 155° , and dissolves in water and alcohol, but not in ether. *Dikippurylhydrazine*, $(\text{NHBz}\cdot\text{CH}_2\cdot\text{CO})_2\text{N}_2\text{H}_2$, can be prepared by heating a mixture of hippurylhydrazine and ethylic hippurate in molecular proportion; it forms small, silvery crystals, melts at $268\text{--}269^\circ$, and is insoluble in boiling alcohol, boiling water, and ether; it is a feeble acid.

Hippurylazoimide, $\text{NHBz}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{N}_3$, the product of the action of sodium nitrite and acetic acid on an aqueous solution of hippurylhydrazine, has been previously described as a nitrosohippurylhydrazine (Abstr., 1891, 57), and as diazohippuramide (Abstr., 1892, 113); new analyses have now established its identity. It does not give Liebermann's reaction, as previously stated, neither does it give a precipitate with silver nitrate in alcoholic solution until some time has elapsed, when silver azoimide separates. With alkalis, hippurylazoimide yields the alkali azoimide and the alkali hippurate, but as an intermediate product a salt is obtained which has a blue fluorescence (compare *loc. cit.*). With acids, hippurylazoimide is hydrolysed into hippuric acid and azoimide, whilst with ammonia it yields ammonium azoimide and hippuramide. This reaction with ammonia is typical of the behaviour of hippurylazoimide with aniline, paratoluidine, and metatoluylenediamine; the following new compounds have been prepared by such reactions.

Hippuranilide crystallises in long, lustrous prisms, melts at $208\cdot5^\circ$,

and dissolves easily in hot glacial acetic acid and hot alcohol, but only sparingly in cold alcohol or ether, and not at all in cold water. *Nitrosohippuranilide*, $\text{NHBz}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NPh}\cdot\text{NO}$, obtained by the action of nitrous acid on the anilide, is a yellowish, crystalline powder, which darkens below 100° , and melts between 195° and 197° .

Hippuroparatoluidide, $\text{NHBz}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\text{Me}$, crystallises in colourless needles, and dissolves freely in hot alcohol and hot glacial acetic acid, but only sparingly in water, cold alcohol, or ether.

Hippuroparatoluylenediamide, $\text{NHBz}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{NH}_2$, crystallises in pale yellow, lustrous laminæ, melts at 205° , and shows a similar solubility to that of hippuroparatoluidide.

The behaviour of hippurylazoimide with hydrazine and acid hydrazides has already been indicated (Abstr., 1895, 34), and the products of these reactions will be described in a future communication.

In discussing the behaviour of hippurazide with water, alcohol, and halogens (compare Abstr., 1894, i, 331; 1895, 32; this vol., i, 34), the author adopts the name *hippenyl* for the radicle $\text{NHBz}\cdot\text{CH}_2$ —.

Dihippenylcarbamide, $(\text{NHBz}\cdot\text{CH}_2\cdot\text{NH})_2\text{CO}$, is obtained when hippurylazoimide is boiled with water, carbonic anhydride and nitrogen being eliminated. It forms microscopic, colourless crystals, melts at 246° , and is nearly insoluble in water, but dissolves to some extent in hot alcohol and glacial acetic acid. Hydrochloric acid, at 120° , converts it into benzoic acid, ammonium chloride, carbonic anhydride, and formaldehyde. When the hot filtrate from the dihippenylcarbamide is cooled, a compound, probably *hippenylcarbanil*,



or a polymeride thereof, separates in the form of colourless crystals, which melt at 233° ; dilute acids readily decompose it into benzoic acid, ammonia, formaldehyde, and carbonic anhydride. A third compound, $\text{C}_9\text{H}_6\text{N}_2\text{O}$, is left as an oil when the mother liquor from the carbanil is evaporated; it is soluble in alcohol and in glacial acetic acid, from which it is precipitated in the form of crystals; it melts at 98° . The same substance is produced when hippurylazoimide is heated either by itself or in an indifferent medium.

Hippurylazoimide reacts with alcohols at their boiling points to form the corresponding hippenylurethanes; these are hydrolysed by hydrochloric acid, at 100° , into benzoic acid, ammonia, formaldehyde, carbonic anhydride, and the parent alcohol. *Hippenylethylurethane*, $\text{NHBz}\cdot\text{CH}_2\cdot\text{NH}\cdot\text{COOEt}$, crystallises in aggregates of colourless needles, melts at 162° , and dissolves easily in hot alcohol, benzene, and glacial acetic acid, but only sparingly in hot water. It behaves as a base, and can be distilled almost unchanged. *Hippenylmethylurethane*, $\text{NHBz}\cdot\text{CH}_2\cdot\text{NH}\cdot\text{COOMe}$, crystallises like the ethyl compound, and melts at the same temperature (162°). *Hippenylbenzylurethane*, $\text{NHBz}\cdot\text{CH}_2\cdot\text{NH}\cdot\text{COO}\cdot\text{CH}_2\text{Ph}$, crystallises in felted needles, which become highly electrified by friction; it also melts at 162° . Both the last-named compounds resemble the ethyl compound in properties.

Alkyl haloid salts react with moist hippurylazoimide, when warmed therewith, to form the corresponding hippenylurethane, with

liberation of hydrogen haloid. In this reaction, the author sees evidence that moist hippurylazoimide has the constitution



By treating hippurylazoimide with a halogen in ethereal solution, nitrogen is eliminated, and a dihaloidhippenylcarbanil is formed. In this way, compounds which are assumed to be *dibromohippenylcarbanil*, $\text{NHBz}\cdot\text{CH}_2\cdot\text{NBr}_2\cdot\text{CO}$, and *diiodohippenylcarbanil* have been crystallised.

Reactions of hippurylazoimide with hydrogen chloride, aldehyde, and acid amides, are briefly mentioned, but their elucidation will receive further attention.

A. G. B.

Appendix to recent Publications (Benzoylhydrazines). By THEODOR CURTIUS (*J. pr. Chem.*, 1895, [2], 52, 272—276).—In describing carbohydrazimine, Curtius and Dedichen (*Abstr.*, 1895, i, 29) have overlooked the fact that Angeli (*Abstr.*, 1894, i, 149) had previously prepared the same compound. The compounds described as hydrazimines in the same paper are wrongly named; they contain two fewer hydrogen atoms, and are identical with Pinner's isodihydrotetrazines (*Ber.*, 1889, 22, 3274). The author thinks Purgotti's claim for priority (*Abstr.*, 1895, i, 27) cannot be allowed.

Ethyl benzoylhydrazineacetate, $\text{COPh}\cdot\text{NH}\cdot\text{N}:\text{CMe}\cdot\text{CH}_2\cdot\text{COOEt}$ (compare Struve, *Abstr.*, 1895, i, 34), has been prepared by heating benzoylhydrazine with ethyl acetoacetate; the crude material melts at about 60° , but when its solution in alcohol is diluted, it separates as an oil, which is still liquid at -15° .

The preparation of ethyl metanitrobenzoylhydrazineacetate (*Abstr.*, 1895, i, 276) is detailed.

A. G. B.

Metallic Bisulphite Compounds of Aldehydes. By A. FAGARD (*J. Pharm.*, 1895, 6, [2], 145—148).—*Benzaldehyde lithium hydrogen sulphite*, $\text{C}_7\text{H}_6\text{O}\cdot\text{LiHSO}_3 + \frac{1}{2}\text{H}_2\text{O}$, is prepared by passing sulphurous anhydride into an aqueous suspension of lithium carbonate, into which benzaldehyde is slowly dropped. The product is evaporated to crystallisation, preferably under low pressure. The sulphate crystallises in small, colourless prisms, and appears to resemble the analogous sodium compound.

Acetone barium hydrogen sulphite, $2\text{C}_3\text{H}_6\text{O}\cdot\text{Ba}(\text{SO}_3\text{H})_2\cdot\text{H}_2\text{O}$, is made by passing sulphurous anhydride into a mixture of barium hydroxide, water, and acetone. The baryta gradually dissolves, with evolution of heat, and the additive compound separates on cooling. It crystallises in small, brilliant plates, resembling those of boric acid.

The corresponding *strontium* compound is anhydrous, and forms small needles, or twinned prisms.

JN. W.

Resolution of Benzaldehydecyanhydrin by means of Alkalis. By CARL GLÜCKSMANN (*Chem. Centr.*, 1895, i, 273—274, from *Pharm. Post.*, 27, 573—574 and 585—588; compare E. Utescher, *Abstr.*, 1895, i, 419).—The fact that benzaldehyde combines with

hydrocyanic acid in dilute solution has no bearing on the question of the hydrolysis of benzaldehydecyanhydrin, since this is treated successively with alkali, acid, and silver nitrate. The action of magnesium hydroxide is, like that of potash, direct; it is not dependent on the formation of silver oxide, and the hydrolysis is completed more rapidly. J. B. T.

Parahydroxybenzaldehyde. By CARL PAAL (*Ber.*, 1895, **28**, 2407—2414).—The monobromo- and moniodo-derivatives of parahydroxybenzaldehyde described by Herzfeld (*Ber.*, **10**, 2196) are in reality disubstitution products. Bromine converts parahydroxybenzaldehyde, when dissolved in dilute alcohol, directly into the dibromo-derivative, whilst, if chloroform be used as the solvent, *metabromoparahydroxybenzaldehyde* [$\text{CHO}:\text{Br}:\text{OH} = 1:3:4$] can readily be obtained. It crystallises from hot water in white plates, melts at 124° , and decomposes when distilled. The *sodium* and *silver* derivatives crystallise in needles. *Metabromoparahydroxybenzaldehyde* crystallises in druses of white needles, melting at 135° . *Metabromoparahydroxybenzylideneaniline* forms flat needles, melting at 135° . *Metabromoparahydroxybenzoic acid* is formed by the oxidation of the aldehyde with alkaline permanganate; it crystallises in concentric groups of white, flat needles, melting at 148° , and is soluble in hot water. *Metiodoparahydroxybenzaldehyde* is found in the mother liquors obtained in the preparation of the di-iodo-derivative. It crystallises in white plates, but has not yet been obtained quite pure.

Metanitroparahydroxybenzaldehyde can be readily prepared by dissolving the hydroxybenzaldehyde in acetic acid and adding nitric acid. A. H.

Ketones. By HEINRICH LIMPRICHT (*Annalen*, 1895, **286**, 306—342).—The ketones described in the following abstracts were prepared by mixing the chloride employed with a slight excess of the hydrocarbon, adding several volumes of carbon bisulphide, and heating the liquid with aluminium chloride in a reflux apparatus for 8—12 hours. The ketone is obtained as a resinous cake, and, after being washed with water, is crystallised from alcohol.

The carbonyl group in these ketones occupies the para-position with respect to the methyl of the tolyl residue. M. O. F.

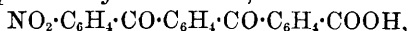
Metanitrophenyl Paratolyl Ketone. By HEINRICH LIMPRICHT and M. LENZ (*Annalen*, 1895, **286**, 307—321).—*Metanitrophenyl paratolyl ketone* crystallises in white leaflets, and melts at 111° ; in small quantities, it may be distilled without undergoing decomposition. The ketone is readily soluble in organic solvents and hot alcohol, but is sparingly soluble in cold alcohol and 50 per cent. acetic acid. The *dichloride* is obtained as a brown oil by heating it with phosphorus pentachloride; the ketone is regenerated on treating this substance with alcoholic ammonia or aniline. The *monochloro*-derivative is formed when chlorine gas is led into the ketone at 150° ; it crystallises from alcohol in long, brittle needles, and melts at 96° . The *monobromo*-derivative crystallises from alcohol in long, white needles, and melts at 116° . *Metanitrophenyl-paratolyl-ketonesulphonic acid* is obtained by

dissolving the ketone in several volumes of fuming sulphuric acid; it crystallises from water in large, rhombic plates containing $3\text{H}_2\text{O}$. The substance effloresces in the atmosphere, and melts at 140° with effervescence, but if heated for eight hours in the vapour of boiling toluene it becomes anhydrous, and then melts at 215° ; the barium salt crystallises from water in colourless prisms, and contains $3\text{H}_2\text{O}$. *Dinitrophenyl paratolyl ketone* forms white scales, and melts at 125° ; the *trinitro*-derivative crystallises in minute, six-sided prisms, and melts at 165° . *Azoxyphenyl paratolyl ketone* is prepared by dissolving the nitroketone in alcoholic potash; it separates from alcohol in yellow crystals, and melts at 145° . The *ketoazime*, obtained by heating the alcoholic solution of the ketone with hydroxylamine hydrochloride and sodium carbonate, crystallises from alcohol in white, lustrous needles, melting at 111° ; if caustic soda is employed, the *ketoazime* of the azoxy-derivative is formed, occurring in two modifications which melt at 235° and 245° respectively.

Metamidophenyl paratolyl ketone is obtained by reducing the nitroketone in alcoholic solution with stannous chloride; it crystallises from alcohol in amber-coloured prisms, melts at 111° , and may be distilled in small quantities without undergoing decomposition. The *hydrochloride* crystallises in needles, and melts at 198° ; the *sulphate* separates from water in aggregates of needles, and melts at 142° . The *sulphonic acid* of the amido-ketone forms small crystals which decrepitate when heated; it melts at 300° , and effervesces and blackens. The *acetyl*-derivative crystallises in small, white prisms, and melts at 139° . On adding sodium nitrite to an aqueous solution of the amidoketone sulphate, the *diazo*-compound is formed: gas is evolved when the diluted liquid is boiled, and the slender, white needles which the cold solution deposits melt at 120° , and consist probably of hydroxyphenyl paratolyl ketone. Phenyl paratolyl ketone is obtained from the amido-ketone by adding a concentrated aqueous solution of sodium nitrite to a solution of the hydrochloride in absolute alcohol, and treating the liquid with finely divided copper. The *ketoazime* of amidophenyl paratolyl ketone crystallises in minute, white prisms, and melts at 146° ; the amido-ketone is regenerated on heating it with concentrated hydrochloric acid for four hours.

Metanitroparabenzoylbenzoic acid, $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{COOH}$, is obtained by oxidising the nitroketone, in glacial acetic acid solution, with chromic anhydride; it crystallises in rhombic tables, melts at 242° , and sublimes at higher temperatures, forming white crystals. The *potassium* salt crystallises in white needles, and the barium salt, containing H_2O , forms leaflets; the *chloride* melts at 94° , and the *amide* at 204° . *Metamidoparabenzoylbenzoic acid* is obtained by reducing the foregoing nitro-compound with stannous chloride; it crystallises from alcohol, and contains H_2O , which is lost at 145° , when the substance melts; the barium salt is anhydrous, the *hydrochloride* crystallises in long, slender needles, melting above 250° , and the *sulphate* contains $2\text{H}_2\text{O}$. When the chloride of nitrobenzoylbenzoic acid is heated with toluene and aluminium chloride, *metanitrophenyl paratolyl-phenylene diketone*, $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{Me}$, is formed; it crystallises in colourless leaflets, and melts at 210° . When oxidised

with chromic anhydride in glacial acetic acid solution, it yields *meta-nitroparabenzoylparabenzoylbenzoic acid*,



which melts at 276°; the *sodium* salt crystallises in nacreous scales.

M. O. F.

Paranitrophenyl Paratolyl Ketone. By HEINRICH LIMPRICHT and E. SAMIETZ (*Annalen*, 1895, **286**, 321—332).—*Paranitrophenyl paratolyl ketone* crystallises in white needles, and melts at 122—124°. In small quantities, it may be sublimed without undergoing decomposition; the ketone is soluble in organic solvents and in concentrated sulphuric acid. *Dinitrophenyl paratolyl ketone* melts at 127°, and *trinitrophenyl paratolyl ketone* at 159°; both these compounds have been obtained by Milne (*Ber.*, 1874, **7**, 983), and they appear to be identical with the dinitro- and trinitro-ketones described in the foregoing abstract.

Paramidophenyl paratolyl ketone is obtained by reducing an alcoholic solution of the nitro-compound with stannous chloride; it separates from benzene in well-formed crystals, and melts at 179°. The *sulphate* forms nacreous leaflets, and melts and decomposes at 210—216°; the *acetyl* derivative melts at 155°. On adding sulphuric acid and sodium nitrite to an alcoholic solution, the amido-ketone becomes diazotised; copper powder is then added, and on filtering the liquid into water, separation of phenyl paratolyl ketone (m. p. 52°) takes place. *Diamidophenyl paratolyl ketone* is obtained by reducing the dinitro-compound, and melts at 178°; the *sulphate* becomes dark, and decomposes above 240°. *Triamidophenyl paratolyl ketone* crystallises from water in white needles, which become brown on exposure to air; it melts at 199°.

Parahydroxyphenyl paratolyl ketone is obtained by boiling an aqueous solution of the diazotised amido-ketone; it crystallises in long, white needles, and melts at 160°. *Bromophenyl paratolyl ketone* is prepared by treating the diazo-compound with hydrogen bromide and copper powder; it crystallises in small, white needles, and melts at 139°. The *ketoime* of paranitrophenyl paratolyl ketone crystallises in aggregates of needles, and melts at 145°; the *phenylhydrazone* crystallises in lustrous, scarlet needles, and melts at 154°. The *phenylhydrazone* of the amido-ketone forms lustrous, brownish-red, rhombic crystals, and melts at 163°.

Paranitroparabenzoylbenzoic acid is obtained by oxidising paranitrophenyl paratolyl ketone with chromic anhydride in glacial acetic acid solution; it melts at 255°. The *sodium* salt crystallises in small, anhydrous leaflets; the *chloride* melts at 124°. *Paramidoparabenzoylbenzoic acid* crystallises in bright yellow needles, and melts at 211°; the *sulphate* is colourless and anhydrous.

Paranitrophenyl paratolylphenylene diketone,



is obtained from toluene and the chloride of paranitroparabenzoylbenzoic acid by treatment with aluminium chloride; it melts at 236°. *Paranitroparabenzoylparabenzoylbenzoic acid* crystallises in lustrous leaflets, and melts at 306—308°; the *sodium* salt dissolves sparingly in water.

M. O. F.

Metanitrophenylxylyl Ketones. By HEINRICH LIMPRICHT and H. FALKENBERG (*Annalen*, 1895, **286**, 333—342).—*Metanitrophenyl metaxylyl ketone* crystallises in lustrous yellow leaflets and melts at 64°. The *trinitro*-derivative crystallises from alcohol in yellow needles and melts at 138—139°.

Metamidophenyl metaxylyl ketone is obtained by reducing the nitro-compound with stannous chloride; it forms brownish crystals and melts at 118°. The *hydrochloride* crystallises in needles and the *sulphate* in lustrous nodules. The *sulphonic acid* of metanitrophenyl metaxylyl ketone crystallises from water in long, white, lustrous needles; the *barium* salt contains 2H₂O, which is lost at 130°. *Azoxyphenyl metaxylyl ketone* is prepared by treating the nitro-ketone with boiling alcoholic potash; it separates from petroleum in small, red needles and melts at 124°. The *ketoxime* of metanitrophenyl metaxylyl ketone forms small, white crystals, and melts between 131° and 149°.

Two *metanitrobenzoylmetatoluic acids*, NO₂·C₆H₄·CO·C₆H₃Me·COOH, are obtained by oxidising the nitro-ketone with chromic anhydride in glacial acetic acid solution, melting at 173° and 152—153° respectively. The *barium* salt of the former is anhydrous, and crystallises in yellow needles and the *silver* salt forms minute white prisms, becoming violet when exposed in the moist state to light; the *chloride* is an oil, and the *amide* forms yellowish-brown crystals and melts at 226°.

Metanitrophenyl orthoxylyl ketone crystallises in yellow plates belonging to the rhombic system, and melts at 100°. *Metamidophenyl orthoxylyl ketone* is very soluble in alcohol and ether; the *sulphate* crystallises in pale-red nodules, and the *hydrochloride* forms white needles.

Metanitrobenzoylorthotoluic acid forms small, yellowish crystals and melts at 191°; the *barium* salt crystallises in yellow needles, and the *silver* salt is also crystalline, becoming violet when exposed to light in the moist condition.

Metanitrophenyl paraxylyl ketone forms white, silky crystals, and melts at 97—98°. *Metamidophenyl paraxylyl ketone* was not obtained in the crystalline state; the *sulphate* forms reddish crystals, and the *hydrochloride* crystallises in yellowish needles.

Metanitrophenylparatoluic acid crystallises from glacial acetic acid in lustrous, brownish needles, and melts at 189°; the *barium* salt forms small, yellow crystals, and the moist *silver* salt is decomposed by light.

M. O. F.

Resacetophenone. By GEORG GREGOR (*Monatsh.*, 1895, **16**, 619—629; compare Nencki and Sieber, *Abstr.*, 1881, 591; Wechsler, *Abstr.*, 1894, i, 521, and Glücksmann, *Abstr.*, 1892, 38).—When diethylresacetophenone (1 mol.) is suspended in water and oxidised by the gradual addition of a solution containing potassium permanganate (1 mol. K₂Mn₂O₈) and potassium hydroxide (2 mols.), 2:3-diethoxybenzoylformic acid, C₆H₃(OEt)₂·CO·COOH, is formed. It is insoluble in cold water but dissolves in hot water, and more readily in alcohol and ether; from the solution in benzene, it separates in small crystals

which melt at 127° . It forms an *oxime*, $C_{12}H_{14}O_4 \cdot NOH$, which crystallises from benzene and melts and decomposes at 130° , a *silver salt*, $C_{12}H_{13}AgO_5$, which is amorphous, a *sodium salt*, $C_{12}H_{13}NaO_5 + 6H_2O$, which crystallises in scales, and a crystalline *barium salt*,



On reduction with sodium amalgam, the alcoholic acid, $C_{12}H_{16}O_5$, is formed. This crystallises from benzene, melts at 115° , forms the *silver salt*, $C_{12}H_{15}AgO_5$, and is oxidised by permanganate in dilute acid solution to an acid identical with the product of oxidation of Tiemann and Lewy's diethylresorcyaldehyde, which is therefore unsymmetrical diethoxybenzoic acid, $OEt \cdot C \begin{smallmatrix} \text{CH} \cdot C(OEt) \\ \text{CH} = \text{CH} \end{smallmatrix} \cdot C \cdot COOH$.

The author therefore concludes that resacetophenone has the constitution $OH \cdot C \begin{smallmatrix} \text{CH} = \text{CH} \\ \text{CH} \cdot C(OH) \end{smallmatrix} \cdot C \cdot COMe$.

G. T. M.

Constitution of Fisetin. By STANISLAUS VON KOSTANECKI and JOSEF TAMBOR (*Ber.*, 1895, **28**, 2302—2309; compare *Abstr.*, 1894, i, 93).—Two constitutional formulæ are possible for fisetin, which is converted by fusion with potash into resorcinol, glycollic acid and protocatechuic acid, $C_6H_3(OH) \begin{smallmatrix} O - C \cdot C_6H_3(OH)_2 \\ CO \cdot C \cdot OH \end{smallmatrix}$, [$OH : O : CO = 1 : 5 : 6$

or $1 : 3 : 4$]. When tetraethylfisetin is boiled with alcoholic potash, it yields diethylprotocatechuic acid and diethyl fisetol ether, which, if fisetin have the second of the above formulæ, must have the formula, $OEt \cdot C_6H_3(OH) \cdot CO \cdot CH_2 \cdot OEt$ [$= 1 : 3 : 4$], according to which it is an ethoxy-derivative of monethyl resacetophenone ether. On oxidation, diethyl fisetol ether is converted into ethyl- β -resorcylic acid (Herzig, *Abstr.*, 1891, 1386). The authors have now shown that ethyl resacetophenone ether yields exactly the same product and have thus confirmed the accuracy of the view that the second of the above formulæ represents the constitution of fisetin. When resacetophenone is treated with alcoholic potash and ethylic iodide, it yields a mixture of the two ethers. *Diethyl resacetophenone ether* crystallises in quadratic prisms melting at $74-75^{\circ}$. *Ethyl resacetophenone ether*, $OEt \cdot C_6H_3(OH)CO \cdot CH_2 \cdot OEt$, separates from dilute alcohol in white plates melting at 49° . On oxidation, the latter of these compounds is converted into ethyl- β -resorcylic acid, identical with that obtained by Herzig from diethyl fisetol ether, and with that prepared by the authors from β -resorcylic acid.

Benzoylresorcinol differs from resacetophenone in its behaviour towards alcoholic potash and methylic iodide, *benzoylmethylresorcinol*, $C_6H_2MeBz(OH)_2$, being formed. This substance crystallises in faintly yellow lustrous plates, melting at 176° ; it does not contain a methoxyl group, and yields a *diacetate*, melting at 120° , and a *dibenzozate*, melting at 149° . The benzoylmethylresorcinol is accompanied by *benzoylmethylresorcinol methyl ether*, $OMe \cdot C_6H_2MeBz \cdot OH$, which crystallises in rhombic tablets, melting at 125° . The *monacetate* melts at 86° .

A. H.

Action of finely divided Silver on Ethylic Phenylbromacetate. By CARL HELL and S. WEINZWEIG (*Ber.*, 1895, **28**, 2445—2454).—Phenylbromacetic bromide was prepared by the action of phosphorus pentabromide (2 mols.) on mandelic acid (1 mol.), and was then converted into the ethylic salt by dissolving it in ethylic alcohol. The authors find that the yield is just as good when one-half or even one-quarter of the theoretical quantity of pentabromide is used; this is due to the fact that the hydrogen bromide which is formed during the reaction also acts on the mandelic acid. The ethylic salt boils at 175° under a pressure of 25 mm., and small quantities may be distilled at ordinary atmospheric pressure without undergoing decomposition.

Finely divided silver acts on the ethylic salt at the ordinary temperature, but the action is greatly accelerated by heating the two together in an oil bath at 170—180°. No product of low boiling point could be isolated, but the ethereal extract yielded a mixture of α - and β -ethylic diphenylsuccinates (compare Reimer, *Abstr.*, 1882, 200), together with a small quantity of some oily ethylic salt which could not be obtained in a state of purity. Both α - and β -salts, when hydrolysed with alcoholic potash, yield Reimer's α -diphenylsuccinic acid, whereas when hydrolysed with hydrobromic acid they both yield the β -acid. The action of silver on ethylic phenylbromacetate is thus similar to its action on α -brominated fatty acids generally, and we may suppose the two isomeric ethereal salts to be formed according to the two general reactions previously given (see this vol., i, 10).
J. J. S.

Reduction of Phenolcarboxylic acids. By ALFRED EINHORN and JOHN S. LUMSDEN (*Annalen*, 1895, **286**, 257—277).—The authors' experiments show that whilst metaphenolcarboxylic acids are converted by reduction into γ -hydroxyhexamethylenecarboxylic acids, the ortho-derivatives generally yield dibasic acids of the pimelic series.

Pimelic acid is formed when salicylic acid is reduced with sodium and amyl alcohol (*Abstr.*, 1894, i, 246). The quantity of this acid, which is formed on reducing ethylic salicylate or its ethyl ether, is extremely small, and probably arises from hydrolysis; the main product of the action consists of hexahydrobenzoic acid. By the action of sodium on ethylic pimelate moistened with alcohol, Dieckmann obtained ethylic β -ketohexamethylenecarboxylate (*Abstr.*, 1894, i, 173), which is converted into ethylic hexahydrosalicylate on reduction. The authors have treated ethylic β -ketohexamethylenecarboxylate dissolved in amyl alcohol with sodium, and obtained pimelic acid. This acid is also formed when guaiacolcarboxylic acid is reduced.

Phenylaceticpropionic acid, $\text{COOH}\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{COOH}$, is obtained by reducing 2 : 3-hydroxynaphthoic acid (m. p. 216°) in the manner indicated; it is also formed when 2 : 1-hydroxynaphthoic acid (m. p. 156°) is reduced, a mixture of *ac*- and *ar*-tetrahydro- β -naphthol being produced at the same time. It crystallises from water in colourless, hexagonal prisms, and melts at 139°; it dissolves

readily in ether and alcohol. The *calcium* and *barium* salts are anhydrous, the *silver* salt darkens slowly in daylight, and the *copper* salt is bright green; the *ethylic* salt is a viscous oil, which has an agreeable odour, and boils at 210—212° under a pressure of 40 mm. *Nitrophenylenaceticpropionic acid* crystallises from water in colourless, lustrous leaflets, and melts at 172°; it is sparingly soluble in cold water, but dissolves more readily in hot water, and is very soluble in alcohol and ether. The *calcium* salt is anhydrous, and the *silver* salt explodes readily when heated. When the calcium salt is submitted to dry distillation, β -ketotetrahydronaphthalene (Abstr., 1894, i, 419) is formed; if the latter is slowly added to boiling dilute nitric acid, phenylenedi-acetic acid is produced. M. O. F.

Isomeric Bromocinnamic acids and Cinnamic acids. By EMIL ERLÉNMEYER (*Annalen*, 1895, **287**, 1—25).—The author's experiments show that Glaser's α - and β -bromocinnamic acids are geometrically isomeric modifications of a bromocinnamic acid having the halogen in the α -position.

By the reduction of Glaser's β -bromocinnamic acid, in alcoholic solution, with zinc dust, an acid has been obtained which resembles Liebermann's isocinnamic acid in every respect except crystallographic form; it belongs to the monoclinic system, $a : b : c = 1.146 : 1 : 2.344$; $\beta = 79^\circ 59'$. On other occasions, reduction of this acid gave rise to a mixture of cinnamic and allocinnamic acids, whilst the exclusive product of Glaser's α -bromocinnamic acid was ordinary cinnamic acid.

Transparent crystals of the new isocinnamic acid (m. p. 44°) rapidly become opaque, and then melt at 68°; this indicates the spontaneous transformation of the substance into allocinnamic acid. Aniline converts both modifications of isocinnamic acid into allocinnamic acid; and the aniline salt of isocinnamic acid (Liebermann, Abstr., 1890, 1417), when treated with alkali, yields allocinnamic acid. Treatment with concentrated sulphuric acid at 50° for 15 minutes converts allocinnamic acid and both modifications of isocinnamic acid into ordinary cinnamic acid.

When allocinnamic acid (0.5 gram) is dissolved in alcohol (5 c.c.), treated with zinc bromide (0.7 gram), and allowed to remain for several days at the ordinary temperature, dilution with 20 c.c. of water causes the separation of an oil which solidifies to crystals, consisting of isocinnamic acid. It seems probable, therefore, that when Glaser's β -bromocinnamic acid is reduced in alcoholic solution with zinc dust, a mixture of allocinnamic with ordinary cinnamic acid is first produced, the former being transformed into isocinnamic acid under the influence of zinc bromide.

Glaser has already shown that the α -bromocinnamic acid of low melting point is converted into the other modification when heated; the author's experiments prove that between the β -bromocinnamic acids the converse change takes place.

The author confirms the description already given by Michael and Browne of the treatment of phenylpropionic acid with hydrogen bromide (compare also Abstr., 1892, 848).

The discovery of a second isocinnamic acid introduces a fourth isomeric phenylacrylic acid. An attempt is made to explain the relationship which exists between these four modifications.

M. O. F.

Condensation of Glyoxylic acid with Amido-acids. By CARL BOETTINGER (*Arch. Pharm.*, 1895, **233**, 199—209).—The amidobenzoic acids condense with glyoxylic acid in alcoholic solution to acids of the composition $\text{COOH}\cdot\text{C}_6\text{H}_4\cdot\text{N}\cdot\text{CH}_2\cdot\text{COOH}$. These are yellow substances; they dissolve in alkaline carbonates, and form *di-silver salts*: the 1 : 2- and 1 : 3-compounds readily lose carbonic anhydride, but the 1 : 4-compound is more stable. No well-defined product was obtained by the action of glycocine on glyoxylic acid. The oxalates of the three amidobenzoic acids are described.

C. F. B.

Benzenesulphonamides and Mixed Secondary Amines. By OSCAR HINSBERG and A. STRUPLER (*Annalen*, 1895, **287**, 220—230; compare *Abstr.*, 1893, i, 168).—*Diphenylsulphonethylenediamine*, $\text{C}_2\text{H}_4(\text{NH}\cdot\text{SO}_2\text{Ph})_2$, is prepared by warming on the water bath a mixture of benzenesulphonamide, concentrated aqueous potash, and ethylenic bromide; it crystallises from alcohol in colourless needles, and melts at 168° .

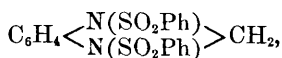
Diphenylsulphonediethylethylenediamine is obtained from the foregoing compound on treating it with potassium hydroxide and ethylic bromide or iodide; it separates from alcohol in minute crystals, and melts at $152\cdot5^\circ$.

Diethylethylenediamine, $\text{C}_2\text{H}_4(\text{NH}\text{Et})_2$, is formed when the sulphone derivative is heated with concentrated hydrochloric acid at 160° (Hofmann, *Jahresbericht*, 1859, 386); the hydrochloride crystallises in colourless needles.

Diphenylsulphonethorphophenylenediamine, $\text{C}_6\text{H}_4(\text{NH}\cdot\text{SO}_2\text{Ph})_2$, is obtained on agitating orthophenylenediamine with benzenesulphonic chloride and excess of potash; it crystallises from glacial acetic acid in slender needles, and melts at 186° .

Tetraphenyldisulphoneorthophenylenediamine, $\text{C}_6\text{H}_4[\text{N}(\text{SO}_2\text{Ph})_2]_2$, is obtained from phenylsulphoneorthophenylenediamine (Lellmann, *Annalen*, **221**, 17) by the protracted action of benzenesulphochloride and soda; it dissolves with difficulty in ordinary solvents, and melts at 150 — 151° .

Diphenylsulphonemethyleneorthophenylenediamine,



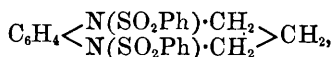
is prepared by adding methylenic iodide to a solution of diphenylsulphonethorphophenylenediamine and sodium ethoxide in alcohol, and heating the mixture until it is neutral; it melts at 147 — 148° , and is converted by hydrochloric acid at 160° into phenylic bisulphide.

Diphenylsulphonethylenethorphophenylenediamine separates from glacial acetic acid in colourless crystals, and melts at 180° .

Ethylenethorphophenylenediamine (tetrahydroquinoxaline) is obtained from the foregoing derivative by treatment with concentrated hydrochloric acid at 160 — 170° (compare Merz and Ris, *Abstr.*, 1887, 722).

The *dinitroso*-derivative crystallises in minute, yellow needles, and melts and decomposes at 168°.

Diphenylsulphonetrimethylenephenylenediamine,



separates from glacial acetic acid in colourless crystals, and melts at 204—205°.

Trimethylenephenylenediamine, $\text{C}_6\text{H}_4 < \begin{matrix} \text{NH} \cdot \text{CH}_2 \\ \text{NH} \cdot \text{CH}_2 \end{matrix} > \text{CH}_2$, is obtained from the foregoing derivative by treatment with concentrated hydrochloric acid at 170°; it melts at 102°, boils at 290—300°, and reduces an ammoniacal silver solution when heated with it. Ferric chloride develops a violet-red colour with the base. The *dinitroso*-derivative melts at 120°.

Diphenylsulphonemetaphenylenediamine crystallises from alcohol or glacial acetic acid, and melts at 194°. When the sodium derivative is treated in alcoholic solution with ethylenic bromide (1 mol.), a compound of the formula $\text{C}_{20}\text{H}_{18}\text{N}_2\text{S}_2\text{O}_4$ is formed; it melts at 190—195°.

M. O. F.

Parabromanilinesulphonic acids: A New Method of Preparing Benzoicsulphinide. By HANS KREIS (*Annalen*, 1895, **286**, 377—388).—*Parabromanilinemetasulphonic acid* [$\text{Br} : \text{HSO}_3 : \text{NH}_2 = 1 : 2 : 4$] is prepared by dissolving parabromacetanilide (30 grams) in fuming sulphuric acid (200 grams) containing 15 per cent. of sulphuric anhydride, and heating the liquid at 140—150° in an oil bath; effervescence takes place, and when this has ceased, the liquid is poured on to 600 grams of ice. The sulphonic acid crystallises from water in slender, white needles containing the solvent, which is eliminated on exposure to air; the *barium* salt is anhydrous. When parabromanilinemetasulphonic acid is reduced with caustic soda and zinc dust, anilinemetasulphonic acid is formed.

Parabromanilineorthosulphonic acid is obtained by heating parabromacetanilide (20 grams) with sulphuric acid (10 grams) at 170—180° for one hour; it crystallises in anhydrous leaflets, and in needles containing $1\frac{1}{2}\text{H}_2\text{O}$.

Parabromocyanobenzeneorthosulphonic acid is obtained from the foregoing substance by means of Sandmeyer's reaction; the *sodium* and *potassium* salts crystallise in colourless, silky needles, and contain $\frac{1}{2}\text{H}_2\text{O}$. The *sulphonic chloride* separates from a mixture of benzene and petroleum in lustrous crystals, and melts at 90°, and the *sulphonamide* is a white powder which melts above 250°; it crystallises from pyridine in leaflets which contain the solvent.

Parabromobenzoicsulphinide is obtained by heating the sulphonamide with aqueous caustic soda; it melts at 227·5° (compare Remsen and Bayley, *Ber.*, 1886, **19**, 835).

Anilineorthosulphonic acid is obtained by eliminating the bromine from parabromanilineorthosulphonic acid by means of caustic soda and zinc dust; from this substance the author has prepared several compounds which have been already described (*Abstr.*, 1893, i, 715), and

records the production of benzoicsulphinide by heating orthocyano-benzenesulphonamide dissolved in 25 parts of water with one molecular proportion of sodium hydroxide. M. O. F.

Formation of Indigo by the Action of Sunlight. By CARL ENGLER and K. DORANT (*Ber.*, 1895, 28, 2497—2501; compare *Ber.*, 3, 885, and *Abstr.*, 1895, i, 231).—An alcoholic solution of orthonitroacetophenone readily condenses with benzaldehyde, in the presence of dilute sodium hydroxide solution, to form *benzylideneorthonitroacetophenone*, $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{CH}\cdot\text{CHPh}$; this crystallises in long, colourless, silky needles, melts at 124° , and forms a *hydrazone* which melts at $146\text{--}147^\circ$. When the ketone is spread on a shallow plate and exposed to bright sunlight, it is rapidly decomposed into indigo and benzoic acid, owing to the oxidising action of the nitro-group on another part of the molecule. No action takes place in the dark, and the rate at which the ketone is converted into indigo depends on the nature of the rays, being greatest when a blue glass plate is interposed between the substance and the sun. Similar intramolecular oxidations have been previously observed by Baeyer (*Abstr.*, 1881, 274; 1883, 341) and by Friedlaender (*Abstr.*, 1895, i, 543).

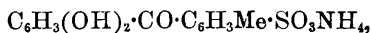
Benzylideneorthoamidoacetophenone is formed when the nitro-ketone is reduced with stannous chloride. It crystallises in prisms which melt at 147° , and its salts are deep red; the *acetyl* derivative melts at 165° , the *hydrazone* at 154° , and a *bromo-derivative* at $159\text{--}160^\circ$. Ferric chloride oxidises the amido-ketone to a substance which melts at $214\text{--}216^\circ$; other products are also formed. When the nitro-ketone is reduced with zinc dust and boiling water, a substance melting at 68° is formed together with the amido-compound. This product is being further examined, as it does not give the reaction of the expected hydroxylamine derivative. J. J. S.

Sulphonephthaleïns. By JOHN WHITE, jun. (*Amer. Chem. J.*, 1895, 17, 545—556; compare *Abstr.*, 1889, 710).—When sulphonefluoresceïn is treated with bromine, a dibromo-substitution product is chiefly formed, and with phosphorus pentachloride a tetrachloro-derivative, which appears to be produced by the displacement of the two hydroxyl groups and the anhydride oxygen in the sulphonefluoresceïn.

It is not possible to prepare sulphonefluoresceïn by the action of resorcinol on orthosulphobenzoic acid, but when an action between these compounds occurs, either four or six residues of resorcinol enter into combination according to the conditions of experimentation.

No pure compounds are described in the paper. A. G. B.

Sulphonephthaleïns from Orthosulphoparatoluic acid. By WALTER JONES (*Amer. Chem. J.*, 1895, 17, 556—569).—*Ammonium paramethyldihydroxybenzoylbenzenesulphonate*,



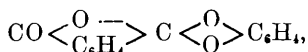
is prepared by heating ammonium hydrogen orthosulphoparatoluic acid (Abstr., 1891, 1228) with resorcinol; it forms colourless crystals, and its aqueous solution yields an insoluble *basic lead salt*, with $12\text{H}_2\text{O}$, when boiled with minium; the corresponding *acid* is obtained by decomposing the lead salt with hydrogen sulphide, and forms colourless crystals, with $4\text{H}_2\text{O}$. The *barium salt* $(\text{C}_{13}\text{H}_{11}\text{SO}_6)_2\text{Ba} + 5\text{H}_2\text{O}$, the normal *lead salt*, with $7\text{H}_2\text{O}$, the *calcium salt*, with $6\text{H}_2\text{O}$, the *zinc salt*, with $x\text{H}_2\text{O}$, and the *silver salt*, with $2\text{H}_2\text{O}$, are described.

Attempts to substitute other acid radicles for the phenolic hydroxyl groups in paramethyldihydroxybenzoylbenzenesulphonic acid proved unsuccessful. When the acid is heated at 170° , it yields *paramethylsulphonefluorescein*, $\text{O} < \begin{smallmatrix} \text{C}_6\text{H}_3(\text{OH}) \\ \text{C}_6\text{H}_3(\text{OH}) \end{smallmatrix} > \text{C} < \begin{smallmatrix} \text{C}_6\text{H}_3\text{Me} \\ \text{O} \end{smallmatrix} > \text{SO}_2$, orthosulphoparatoluic acid, and water; treatment of this fluorescein with phosphorus pentachloride, produces a *tetrachloro*-derivative, and treatment with excess of bromine, produces a dibromo-substitution product which fluoresces like eosin.

Two other sulphonephthaleins can be derived from orthosulphoparatoluic acid, by treating it with resorcinol; one containing four and the other six resorcinol residues.

A. G. B.

Allofluorescein. By BRONISLAW PAWLEWSKI (*Ber.*, 1895, 28, 2360—2362; compare Abstr., 1895, i, 219).—*Allofluorescein*,



is obtained by heating resorcinol with phthalic chloride alone or in solution, on the water bath; the red or yellow product is then treated with acetic anhydride for several hours at 150 — 170° , and, after evaporating the liquid, the residue is repeatedly extracted with glacial acetic acid and with alcohol. The colourless, amorphous substance melts at 140° , and is almost insoluble in the majority of organic solvents; it dissolves to some extent in boiling glacial acetic acid, and to a greater degree in acetic anhydride and ethylic acetate, separating from solution in the amorphous state. The freshly prepared substance dissolves readily in alkalis and alkali carbonates, the liquid exhibiting strong fluorescence; the dried or fused substance, however, dissolves in concentrated alkalis with great difficulty. The fluorescence of solutions in ammonia or barium hydroxide is green.

The paper contains a detailed comparison of allofluorescein with the ordinary modification.

M. O. F.

Relation of the Indulines to the Safranines. By OTTO FISCHER and EDUARD HEPP (*Ber.*, 1895, 28, 2283—2289).—Phenosafra-nine belongs to the same group of compounds as the mauveines, indulines, and indazines. On treatment with alkalis, it yields safranin, or hydroxyaposafranine, which only contains one hydroxyl-group, so that phenosafra-nine must itself be free from water, at all events at 100° . Aposafranine, which is obtained from phenosafra-nine by the removal of the amido-group, therefore, is to be looked on as the simplest meso-phenyl derivative of the series, corresponding with

rosinduline, its formula being
$$\begin{array}{c} \text{CH:CH}\cdot\text{C}\equiv\text{N}\cdot\text{C}\cdot\text{CH}\cdot\text{CH} \\ \text{NH}\cdot\text{C}\cdot\text{CH}\cdot\text{C}\cdot\text{NPh}\cdot\text{C}\cdot\text{CH}\cdot\text{CH} \end{array}$$
 The facts, which, previously, were apparently at variance with this view, have now been more accurately investigated. The free base itself is free from water, like phenosafranine (Abstr., 1895, i, 608), and the benzoyl derivative is also anhydrous. This substance crystallises from benzene in dark violet plates, which contain 1 mol. of benzene; it is strongly basic, and forms yellow salts. The relation between aposafranine and the simplest benzene-induline, appears to be precisely similar to that between aposafranone and the simplest benzeneindone. When aposafranone is heated with aniline and aniline hydrochloride, it is converted into the substance previously termed benzeneindone (*Annalen*, 1884, **226**, 254), and formulated as $\text{C}_{18}\text{H}_{12}\text{N}_2\text{O}$. The formation of this substance from aposafranone now shows that its true formula must be $\text{C}_{24}\text{H}_{17}\text{N}_3\text{O}$, and it is, therefore, *anilidoaposafranone*. When it is boiled with 75 per cent. sulphuric acid, it is converted into *hydroxyaposafranone*, $\text{C}_{18}\text{H}_{13}\text{N}_2\text{O}_2$, which was previously described as benzeneindonehydrate. Hydroxyaposafranone is also formed when aposafranone is boiled with alcoholic potash. Anilidoaposafranone may be reconverted into aposafranone by boiling with 60 per cent. acetic acid and zinc dust. In the same way, the simplest induline derived from aposafranine, which is known as anilidoaposafranine (Kehrmann) may be reconverted into aposafranine.

Phenylinduline, which is derived from benzeneindone by the displacement of a single atom of hydrogen by the anil-group, must now receive the formula $\text{C}_{30}\text{H}_{22}\text{N}_4$, instead of that previously assigned to it, and all the indulines must be classed as anilidosafraanines, their formulæ being altered in accordance with this relationship.

A. H.

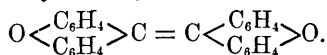
Action of Alkalis on Paranitrotoluenesulphonic acid. By OTTO FISCHER and EDUARD HEPP (*Ber.*, 1895, **28**, 2281—2283; compare Abstr., 1893, i, 697). The authors, in reply to Bender's criticism (Abstr., 1895, i, 287), maintain the accuracy of the results obtained by them in the reduction of paranitrosostilbenedisulphonic acid by means of ferrous sulphate, and its oxidation by chromic acid, new experiments having given the same results as the ones previously quoted.

A. H.

Synthesis of Bidiphenyl and its Identification as Benzerythrene. By ARTHUR A. NOYES and ROLFE M. ELLIS (*Amer.Chem. J.*, 1895, **17**, 620—622).—*Parabidiphenyl*, $\text{PhC}_6\text{H}_4\cdot\text{C}_6\text{H}_4\text{Ph}$, was prepared from parabromodiphenyl by boiling an ethereal solution of it with sodium; the solid matter was separated, washed with water and benzene, and sublimed. It forms large, crystalline laminae, melts at 317° , and distils at 428° (18 mm. pressure); it is insoluble in boiling alcohol, ether, chloroform, and carbon bisulphide; boiling benzene dissolves it sparingly. The compound termed benzerythrene, $\text{C}_{24}\text{H}_{18}$, by Schmidt and Schultz (*Annalen*, 1880, **203**, 18), and obtained by the action of heat on benzene, melted at 308° , and was insoluble in alcohol, but slightly soluble in boiling benzene. The

authors conclude that benzerythrene is identical with parabidi-phenyl.
A. G. B.

Reduction Product of Xanthone. By G. GURGENJANZ and STANISLAUS VON KOSTANECKI (*Ber.*, 1895, **28**, 2310—2311).—When xanthone is boiled with acetic acid and zinc dust, it is converted into dixanthylene (tetraphenyleneethylenedioxide),



This crystallises from benzene in long, thick, almost white needles, which melt at 315°. The solution in benzene has a bluish-green fluorescence. 4:5-Dimethylxanthone is converted by similar treatment into 4:5:4':5'-tetramethyldixanthylene, which does not melt below 360°. 2:7-Dimethylxanthone yields 2:7:2':7'-tetramethylxanthylene which sublimes without decomposition at 275—277°.

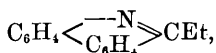
A. H.

Benzylidene-β-dinaphthyl Oxide. By E. MERCK (*Chem. Centr.*, 1895, i, 431; from *Ber. ü. d. Jahr.*, 1894, 21—22).—The residue obtained during the preparation of benzoyl-β-naphthol contains benzylidene-β-dinaphthyl oxide (m. p. 188—191°); it must have been formed from benzaldehyde or benzylidene chloride contained in the benzoic chloride employed.
J. B. T.

Synthesis of Phenanthridine. By AMÉ PICTET and A. HUBERT (*Chem. Centr.*, 1895, 432—433; from *Arch. sci. phys. Genève*, 1894, **32**, 493—504).—The method employed consists in the condensation, by means of zinc chloride, of acidyl orthoamidodiphenyl derivatives, $\text{RNH} \cdot \text{C}_6\text{H}_4\text{Ph}$. Orthoamidodiphenyl is most readily prepared by Graebe and Rateanu's method (*Abstr.*, 1894, i, 529).

2-Formylamidodiphenyl, $\text{COH} \cdot \text{NH} \cdot \text{C}_6\text{H}_4\text{Ph}$, crystallises in colourless needles, melts at 75°, and, when heated with zinc chloride (5 parts) at 280—300°, yields phenanthridine. Mesomethylphenanthridine, $\text{C}_6\text{H}_4 < \overset{\text{N}}{\text{C}} \text{CMe}$, is formed in a similar manner at 320° from acetylamidodiphenyl; it crystallises in small, colourless needles, and melts at 85°. The hydrochloride and mercuriochloride are colourless, and melt at 285° and 247° respectively. The picrate and methiodide are yellow, and melt at 233° and 263° respectively. The platinochloride $(\text{C}_{14}\text{H}_{12}\text{N})_2\text{PtCl}_6 + 2\text{H}_2\text{O}$ (m. p. 272°) is flesh-coloured; the dichromate is orange-yellow, and darkens at 150°; the aurochloride (m. p. 163—164°) is pale yellow. All these derivatives crystallise in needles.

2-Propionylamidodiphenyl crystallises in colourless, lustrous needles; it melts at 65°, and yields mesoethylphenanthridine,



which is deposited from light petroleum in small, colourless needles melting at 54—55°. The following derivatives crystallise in needles.

The *hydrochloride* and *mercurochloride*, melting at 205° and 214° respectively; the *dichromate* is golden yellow; the *picrate* is pale yellow, slowly decomposes when heated, and melts at about 210° ; the *platinochloride*, $(C_{15}H_{13}N)_2, H_2PtCl_6 + 2H_2O$, and the *aurochloride*, are yellow, and melt at 241 — 242° and 149° respectively.

2-Benzoylamidodiphenyl, $NHBz \cdot C_6H_4Ph$, crystallises in pearly, lustrous plates, melts at 85 — 86° , and at 300 — 360° yields *mesophenylphenanthridine*, $C_6H_4 < \overset{\text{---}N}{\text{C}_6\text{H}_4} > CPh$, which is also formed by heating a mixture of amidodiphenyl, benzoic acid, and zinc chloride; it crystallises in iridescent, transparent, quadratic plates, melts at 109° , boils above 360° , is a feeble base, and dissolves in dilute mineral acids with a violet fluorescence. Its salts are only stable in presence of acid; they are decomposed by water. The *hydrochloride*,



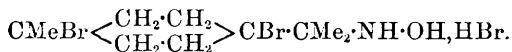
crystallises in yellow prisms melting at 95 — 96° ; the anhydrous compound forms pale yellow needles, and melts at 220° . The *platinochloride* crystallises with $2H_2O$ in yellow needles, and decomposes at about 300° . *Orthodiphenylurethane*, $C_6H_4Ph \cdot NH \cdot COOEt$, prepared from orthamidodiphenyl and ethylic chlorocarbonate crystallises in colourless needles, melts at 186° , and, when heated with zinc chloride, yields phenanthridone.

J. B. T.

Orientation in the Terpene Series. By ADOLF VON BAEYER and FRITZ BLAU (*Ber.*, 1895, **28**, 2289—2297; compare *Abstr.*, 1894, i, 252).—1-Bromo- $\Delta^{4,8}$ -terpene is formed when Wallach's terpene tribromide is dissolved in a mixture of alcohol and ether, and treated with zinc-dust; it forms compact rhombic prisms, melting at 34 — 35° . Hydrogen bromide converts it into dipentene dihydrobromide, along with an oily substance. When bromoterpene is treated with sodium nitrite and hydrobromic acid, the *nitrosobromide* is formed in blue crystals, which melt at 44° , but could not be obtained quite pure.

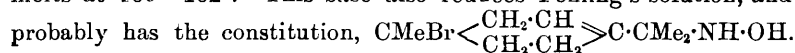
$\Delta^{4,8}$ -Terpenol acetate also yields a *nitrosobromide*, which crystallises in blue needles, and melts at 81 — 82° .

The two nitroso-bromides just described yield the same product when they are treated with a solution of hydrogen bromide in acetic acid, bromine being in both cases set free. This product crystallises in thin, quadratic plates, which melt at 182 — 184° , its constitution being most probably expressed by the formula,



It reduces silver salts and Fehling's solution.

When this substance is dissolved in water, and potash or ammonia added, 2 mols. of hydrogen bromide are removed, and a base, $C_{10}H_{18}NOBr$, is obtained, which crystallises in indefinite forms, and melts at 100 — 102° . This base also reduces Fehling's solution, and probably has the constitution,



Nitrous acid converts it into a nitroso-compound, $C_{10}H_{17}BrN_2O_2$, which crystallises in serrated, rhombic tablets, melting at $138-139^\circ$. This substance may be obtained by a similar series of reactions from each of the three compounds, the nitrosobromide of bromoterpene, the nitrosobromide of terpenol, and the nitrosochloride of terpenol acetate, a fact which confirms the formulæ proposed.

The product of the action of hydrogen bromide on the nitrosochloride of terpenol acetate has the formula, $C_{10}H_{20}NOClBr_2$, and crystallises in almost rectangular tablets melting at $179-180^\circ$.

The hydroxylamine derivative, $C_{10}H_{18}NOBr$, which is formed from the nitrosobromide by the action of hydrogen bromide, is converted by the action of bromine into the original nitrosobromide, so that the action is a reversible one.

Trihydroxyterpane, $C_{10}H_{20}O_3$, is formed by the action of dilute potassium permanganate solution on $\Delta^{4,8}$ -terpenol. It forms crystals which contain 1 mol. water, and melts at $95-96^\circ$. The anhydrous substance melts at $110-112^\circ$, and boils at 200° (pressure = 20 mm.) almost without decomposition. Hydrobromic acid converts it into Wallach's tribromide.

A considerable amount of a substance which melts at $127-128^\circ$, and has the formula of dipentene tetrabromide, is formed during the preparation of the tribromide from dipentene dihydrobromide.

A. H.

From Pinene to Carvacrol. By JOHN L. MEAD and EDWARD KREMERS (*Amer. Chem. J.*, 1895, **17**, 607-611).—Urban and Kremers have already shown that "nitrosopinene" is really an oxime, and that it yields an oil, $C_{10}H_{14}O$, on hydrolysis (*Abstr.*, 1894, i, 468). It is now shown that this oil is carvacrol (compare von Baeyer, *Abstr.*, 1895, i, 379).

A. G. B.

Ethereal Oils. By EDUARD GILDEMEISTER (*Arch. Pharm.*, 1895, **233**, 174-189).—The oil expressed from the rind of sweet limes (*Citrus Limetta* Risso), growing in South Europe, was found to contain limonene with possibly a little phellandrene; also, in smaller amount, linalyl acetate, together with a little linalöl; it thus resembles oil of bergamot, which contains dipentene in addition. The sample examined was brownish-yellow, had the sp. gr. = 0.872 at 15° , and $[\alpha]_D^{20} = +66^\circ 52'$. Linalöl was identified by oxidising it with chromic mixture to geranaldelyde, and converting this, by Doebner's method (*Abstr.*, 1894, i, 261), into citryl- β -naphthocinchonic acid, melting at 197° .

Four samples of oil of origanum from Smyrna were examined; their exact botanical origin was unknown, perhaps they were obtained from *Origanum smyrnaicum*. The sp. gr. was 0.916-0.932 at 15° ; the rotation in a length of 100 mm. $-7^\circ 52'$ and $-8^\circ 44'$ in two of the samples; the percentage of phenols (by shaking 10 c.c. of the oil with 50 c.c. of 5 per cent. soda, and noting the volume of the residual oil) 32.47; all the samples dissolved in $2\frac{1}{2}$ parts of alcohol of 70 per cent. strength by volume. The oil was found to consist mainly of linalöl; cymene is also present, and possibly an "olefinic terpene" (compare Semmler, *Abstr.*, 1891, 655, and Chapman,

Trans., 1895, 58); the phenol present is mainly carvacrol, but there is a small quantity of a phenol that gives a violet colour with ferric chloride. Carvacrol was identified by means of its phenylic cyanate derivative (Goldschmidt, Abstr., 1893, i, 723); cymene by oxidising it with potassium dichromate and dilute sulphuric acid on the water bath to hydroxypropylbenzoic acid, melting at 156—158°, and converting this by boiling with fuming hydrochloric acid into isopropenylbenzoic acid, melting at 255—260° (Wallach, *Annalen*, 264, 10).

C. F. B.

Oil of Lignaloës. By PHILIPPE BARRIER and LOUIS BOUVEAULT (*Compt. rend.*, 1895, 121, 168—170).—Oil of lignaloës contains, in 1000 parts, 1 part each of a bivalent terpene, a quadrivalent terpene, and methylheptenone, 20 parts of licarhodol, 30 parts of a sesquiterpene, and 900 parts of licareol. The sesquiterpene, $C_{15}H_{24}$, boils at 135—136° under a pressure of 10 mm., has a faint, pleasant odour, and combines with 4 atoms of bromine; its proportion varies considerably in different specimens of the oil. The methylheptenone is always present in the oil, and is identical with the methylheptenone obtained by Wallach by the decomposition of cinoleic anhydride; it is isomeric with that found in oil of lemon-grass (Abstr., 1894, i, 491), and, when heated with zinc chloride, is converted into dihydrometaxylene, C_8H_{12} , boiling at 134°. A small part of the licareol is present in the oil in combination with acetic acid and higher acids of the same series.

C. H. B.

Oxidation of Inactive Campholenic acid. By AUGUSTE BÉHAL (*Compt. rend.*, 1895, 121, 213—216).—When oxidised with nitric acid of sp. gr. 1.27, inactive campholenic acid yields hydroxycamphoronic acid, melting at 167—168°, isobutyric acid, and two dibasic acids, $C_7H_{12}O_4$ and $C_6H_{12}O_4$.

The acid $C_7H_{12}O_4$ is very soluble in water, benzene, or ether, crystallises from a mixture of benzene and light petroleum, and melts at 83.5°. Its calcium salt, $C_7H_{10}O_4Ca + 3H_2O$, crystallises in flattened, orthorhombic prisms. The anhydride melts at 38.5°, and boils at 270°; in présence of benzene, it reacts with aniline, and yields the compound $C_6H_{11}O_2 \cdot CO \cdot NPh$, which crystallises from dilute alcohol, melts at 146°, and, when distilled with water, is converted into the imido-compound, $C_5H_{10} \begin{smallmatrix} CO \\ < \\ CO \end{smallmatrix} NPh$, which melts at 121.5°. The acid $C_7H_{12}O_4$ seems to be a glutaric derivative; its ethylic salt boils at 235—238°.

The acid $C_6H_{10}O_4$ melts at 144°, and is very soluble in water; its ethylic salt boils at about 230°, and its anhydride at about 220°; the phenylamido-derivative melts at 185°, and the phenylimido-derivative at 86°.

C. H. B.

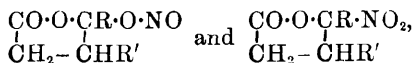
Action of Nitric Peroxide on Campholenic acid. By AUGUSTE BÉHAL and VICTOR BLAISE (*Compt. rend.*, 1895, 121, 256—259).—When nitric peroxide is passed over inactive campholenic acid until the latter has absorbed a molecular proportion of it, a blue liquid is formed, and when this is treated with a cold saturated

solution of potassium hydrogen carbonate, a blue oil remains undissolved and soon solidifies. When this product is dried and crystallised from alcohol of 80°, *ceruleonitrosocampholenolide*, $C_{10}H_{15}NO_3$, is obtained in thin lamellæ, which melt at 134.5°, and have a blue colour similar to that of copper sulphate. It has a neutral reaction, and is insoluble in alkali hydrogen carbonates. If an alcoholic solution is exposed to diffused light for some days, a white, amorphous modification, *leuconitrosocampholenolide*, separates. Unlike the blue compound, it is insoluble in ordinary organic solvents, but when heated with them, or alone, it is reconverted into the blue modification, of which it seems to be a polymeride, although its molecular weight could not be determined.

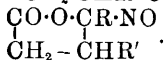
Ceruleonitrosocampholenolide, when treated with alcoholic potash, yields a red azo- or azoxy-derivative, which is decolorised by sodium amalgam, and regenerated by oxidation with mercuric oxide. The product of reduction by the amalgam reduces Fehling's solution in the cold. When boiled with tin and acetic acid, the *ceruleonitrosocampholenolide* yields an unsaturated lactone, which melts at 31.5°, and an amine acetate, which melts at 97°.

Excess of nitric peroxide converts campholenic acid into the compound $C_{10}H_{15}NO_4$, which melts at 175°, and has been described by several previous observers as nitrocampholenic acid. It has, however, no acid function; it is neutral to litmus, and does not decompose alkali hydrogen carbonates. When boiled with potassium hydrogen carbonate, it yields didehydrocampholenolide, $C_{10}H_{14}O_2$, a crystalline compound, which melts at 31.5°, and boils at 193° under a pressure of 17 mm. When boiled with alkali hydroxides, it is converted into dihydroketocampholenic acid, $C_{10}H_{16}O_3$, which crystallises from benzene or dilute alcohol in prismatic needles, and melts at 126° if heated rapidly, or at 112° if kept at this temperature for some time. It begins to change into a lactone above 100°, and at 150°, it yields the original lactone. The acetate of the amine, obtained by reduction of so-called nitrocampholenic acid, crystallises well from absolute alcohol, and melts at 97°.

It would seem that the so-called nitrocampholenic acid is really a nitrocampholenolide; it has a lactonic function, and the NO_2 group seems to exist in two forms, which are probably tautomeric,



the constitution of the lactone and amine being analogous, although the position of the ethylene linking is somewhat uncertain. The ketonic acid probably has the constitution $\text{COOH} \cdot \text{CH}_2 \cdot \text{CHR}' \cdot \text{COR}$, and *ceruleonitrosocampholenolide* the constitution



C. H. B.

Campholic acid. By GUERBET (*Ann. Chim. Phys.*, 1895, [7], 4, 239—365).—The greater part of the work contained in this paper has previously been published (compare Abstr., 1894, i, 254; 1895, i, 61, 240, 295, and 383. Also Errata, Abstr., 1892, 1345; 1893,

i, 108). It is shown that campholic acid is practically not acted on by hydrochloric or hydrobromic acid at 200° .

Campholene hydriodide (Abstr., 1894, i, 254) melts at about 52° when rapidly heated.

The nitrosochloride (Béhal, Abstr., 1895, i, 240) forms an indigo-blue crystalline mass, and melts at 25° when rapidly heated. The author thinks most of his results support the hydroxyketone formula of campholic acid suggested by Friedel. J. J. S.

Gedanite, Succinite, &c. By OTTO HELM (*Arch. Pharm.*, 1895, 233, 191—199; compare Tschirch and Aweng, Abstr., 1895, i, 384).—Gedanite does not contain free succinic acid, although Aweng states that it does; the dealer had, doubtless, sent him as gedanite what was really a specimen of succinite (ordinary amber). Gedanite further differs from succinite in that it contains 2—3 per cent. more carbon and about as much less oxygen; it contains some sulphur, but less than succinite does. A much larger proportion of gedanite dissolves in various solvents than is the case with succinite; it is even entirely soluble in linseed oil. There is a variety of succinite known as "soft" or "friable amber" ("*mürber Succinit*"), which is intermediate in its properties between gedanite and true succinite.

C. F. B.

Opoponax from Burseraceæ. By A. BAUR (*Arch. Pharm.*, 233, 209—252).—The substance once known by this name had a rather unpleasant odour, and was probably derived from a Persian member of the *Umbelliferae*. The substance now known as opoponax contains a pleasant smelling ethereal oil, which is used as a perfume; the samples examined by the author contained plant fragments which showed them to be derived from some member of the genus *Balsamodendron*, order *Burseraceæ*—probably from *B. Kafal*. It contains 19 parts per cent. of resin, 6.5 of ethereal oil, and 70 of gum, besides plant fragments. The resin contains α -panax-resen, $C_{32}H_{54}O_4$, soluble in light petroleum; β -panax-resen, $C_{32}H_{52}O_5$, insoluble in light petroleum, but soluble in ether; and panaresinotannol, $C_{34}H_{50}O_8$, insoluble in light petroleum, and only slightly soluble in ether, but soluble in alcohol, and also, unlike the preceding two, in alkalis. These are yellowish-brown substances, which can be powdered when cold, but are plastic when warm; it was not found possible to hydrolyse them, nor could well-characterised substances be obtained from them in any way. The ethereal oil possibly contained a terpene; the portion of higher boiling point yielded, when hydrolysed, an alcohol, $C_{26}H_{46}O$, boiling at 250 — 255° (uncorr.), and, apparently, a fatty acid (? butyric). This oil is obtained from the drug by treating it with superheated steam; the residue then contains a new substance which is not present in the original drug. This is *chironol*, $C_{28}H_{48}O$, a white, crystallised substance, soluble in ether and hot alcohol, and melting at 176° (uncorr.); it yields crystallised *monacetyl* and *monobenzoyl derivatives*, melting respectively at 196° and 186° (uncorr.), and is oxidised by permanganate in hot acetic acid solution to *chironolic acid*, $C_{28}H_{46}O_4$, a white, amorphous substance, which melts at 100 — 108° , dissolves in alkalis, but not in water; and, in alcoholic solution, reddens litmus

paper. Opoponax also contains an alkaloïd, which could not, however, be obtained crystallised. Unlike the oils from Persian *Umbelliferae*, it contains no umbelliferone and no sulphur.

Mecca balsam also contains resins resembling those of opoponax in character; resins, that is, that cannot be hydrolysed, and so cannot have the constitution of ethereal salts. To "indifferent" resins, which have the character neither of ethereal salts, acids, nor alcohols, Tschirch has given the name of "resens." C. F. B.

Sagapen. By M. HOHENADEL (*Arch. Pharm.*, 1895, **233**, 259—286).—This substance is obtained from the stems and fruits of a Persian species of *Ferula*, order *Umbelliferae*, as was shown by an examination of the plant fragments contained in the drug. The sample examined by the author contained resin, 56·8; ethereal oil, 5·8; water, 3·5; gum, 23·3; and impurities 10·6 per cent. The purified resin is yellowish-brown, and is brittle when cold, plastic when warm, melting at 74—76°; it yields a sublimate of umbelliferone when heated, and, when hydrolysed by boiling with sulphuric acid, it is decomposed into umbelliferone and sagaresinotannol, of which two substances it is the ethereal salt. *Sagaresinotannol*, $C_{24}H_{28}O_5$, is a brown substance soluble in alkalis, and yielding a precipitate with ferric chloride; it yields *monacetyl* and *monobenzoyl derivatives*, and is oxidised by nitric acid to styphnic acid (trinitroresorcinol). The 56·8 parts of purified resin contains 40 of sagaresinotannol, 15·7 of combined, and 0·11—0·15 of free umbelliferone. The ethereal oil contains 9·7 per cent. of sulphur, and probably contains an ethereal salt of valeric acid; the bluish fraction boiling at 210—270° was found to resemble, as regards its absorption spectrum, the similar bluish or greenish fractions, of much the same boiling point, obtained from the oils of galbanum, asafoetida, chamomile, valerian, Japanese valerian, millefoil, absinth, and *Inula Helenium*. The substance contained in it, "azulene," is not, however, present in the original oil, but is formed during the process of fractionation. C. F. B.

Digitalin. By HEINRICH KILIANI (*Arch. Pharm.*, 1895, 299—310).—"The glucosides obtained from the seeds of *Digitalis purpurea* consist, to the extent of at least one-half, of digitonin, which can easily be obtained crystallised" by digesting *Digitalinum pur. pulv. germanic.* with four times its weight of 85 per cent. alcohol. "They contain *Digitalinum verum* (digitalin) as the essential constituent, to which alone their action on the heart is due; the existence of 'digitaleïn' is, to say the least, doubtful. In addition they contain a well-crystallised organic compound containing calcium and potassium. Digitonin and *Digitalinum verum* are both, when pure, very sparingly soluble in water. The ready solubility of the mixture of glucosides (*Digitalinum pur. pulv.*) is due solely to the presence of resinous amorphous substances, in addition. Digitogenin was not detected in Merck's samples. It is certain that the crystals, which Schmiedeberg described as digitin, were nothing but digitonin."

The author has worked out the following method, by means of which *Digitalinum verum* is now prepared on the large scale:—

"One part by weight of *Digitalinum pur. pulv.* is dissolved, by means of a gentle heat, in four of 95 per cent. alcohol. The cold solution is stirred or shaken, and five parts of ether (sp. gr. 0.72) are, meanwhile, added, and the whole allowed to remain for 24 hours in a closed vessel. The alcohol-ethereal solution is then drawn off, weighed or measured, and the weight of solid matter in it (= A) determined by evaporating a portion. The ether and most of the alcohol are then distilled off under reduced pressure until the weight of the residual solution is 1.6 A; 2.4 A parts of water are then added, and the mixture is allowed to stand for 24 hours in a closed vessel. The crude digitalin which has separated is now brought on to a filter, allowed to drain without suction being applied, washed with 10 per cent. alcohol, and, finally, with water, and dried on porous plates or in a vacuum. The dry substance is then 'recrystallised' from 95 per cent. alcohol, with the addition of animal charcoal." It is thus obtained in white granules. C. F. B.

β -Digitoxin. By HEINRICH KILIANI (*Arch. Pharm.*, 1895, 233, 311—320).—The leaves of *Digitalis purpurea* contain neither digitonin nor digitalin, but a new glucoside, β -digitoxin, $C_{28}H_{46}O_{10} + 5H_2O$, can be obtained from them by successive extraction with water and 50 per cent. alcohol. This is contained more largely in the alcoholic extract; the total yield of the pure substance was about 1 gram per kilo. of the leaves. It forms white crystals, which, when anhydrous (from chloroform-alcohol solution), are still unmelted at 240° , but otherwise (from 85 per cent. alcohol) soften at 145 — 150° . When hydrolysed with alcoholic hydrochloric acid, it yields β -digitogenin, $C_{21}H_{32}O_4$, and a substance, *digitoxose*, which crystallises after the manner of glucose, but was found, unexpectedly, to have the composition $C_6H_{12}O_4$.

Schmiedeberg's "digitoxin" was probably an impure specimen of the substance described above; the author proposes to call it, provisionally, α -digitoxin, distinguishing his own compound by the prefix β . C. F. B.

Quassole, a Substance accompanying Quassin. By E. MERCK (*Chem. Centr.*, 1895, i, 435; from *Ber. ü. d. Jahr.*, 1894, 19—20).—*Quassole*, $C_{40}H_{70}O + H_2O$ (?), is obtained from crude quassin by extraction with ether; it crystallises in colourless plates, and melts at 149 — 151° . In a mixture of ether and chloroform $[\alpha]_D = -42.6^\circ$, and in chloroform alone = -46° . In alcoholic solution, it gives a pale yellow coloration with ferric chloride; in chloroform solution, a deep red coloration with concentrated sulphuric acid, and differs from quassin by its absence of taste. Quassole dissolves in fuming nitric acid, but the ordinary concentrated acid is apparently without action.

J. B. T.

Artemisin, a Substance accompanying Santonin. By E. MERCK (*Chem. Centr.*, 1895, i, 436; from *Ber. ü. d. Jahr.*, 1894, 3—6).—*Artemisin*, $C_{13}H_{18}O_4$, is obtained from the last mother liquors in the technical treatment of the seed of *Artemisia maritima*. It is freed from santonin by recrystallisation from chloroform, being deposited

in combination with 1 mol. of the solvent, which is evolved at 90° . It melts at 200° , gradually turns yellow in the air, and is more readily soluble in water and dilute alcohol than santonin; $[\alpha]_D = -84.3^{\circ}$. The ferric chloride reaction is not characteristic; when heated with soda (10 parts) and water (40 parts), a fugitive carmine-red coloration is produced, and, like santonin, it gives the same colour with alcoholic soda. Artemisin is apparently a hydroxysantonin.

J. B. T.

Physcihydrone and Protophyscihydrone. By OSWALD HESSE (*Annalen*, 1895, **286**, 376; compare Abstr., 1895, i, 300).—Physcihydrone has the composition $C_{15}H_{14}O_4$, and protophyscihydrone the formula $C_{15}H_{12}O_4$.

M. O. F.

Phenylcoumalin and Pseudodicotoïn. By OSWALD HESSE (*Ber.*, 1895, **28**, 2507—2509).—In reply to Ciamician and Silber (Abstr., 1895, i, 554), the author states that he was the first to show that "dicotoïn" is a compound of cotoïn and phenylcoumalin. The melting point of phenylcoumalin is still given as 61° , whereas Ciamician and Silber give 68° . The investigation of Tod's pseudo-dicotoïn cannot be continued for lack of material.

J. J. S.

Derivatives of Cinchomeronic acid. By SIEGFRIED BLUMENFELD (*Monatsh.*, 1895, **16**, 693—720; compare Meyer, Abstr., 1894, i, 425, and Pollak, Abstr., 1895, i, 391).—*Diethylic cinchomerionate*, $C_5NH_3(COOEt)_2$ is conveniently prepared by the further ethylation of Strache's ethylic hydrogen cinchomerionate (compare Abstr., 1890, 1157). It is a colourless, odourless oil, having a burning taste and turning yellow on exposure to light; it decomposes when distilled under ordinary pressure, boils at 172.1° (corr.) under a pressure of 21 mm., and does not solidify at -60° . It mixes with alcohol, ether, benzene, xylene, and light petroleum in all proportions, gives a *platinochloride*, $2C_5NH_3(COOEt)_2 \cdot H_2PtCl_6$, which crystallises in small, yellow needles, and melts and decomposes at $142-144^{\circ}$. It forms alkyl additive products, which, on hydrolysis with silver oxide, yield the ethylbetaine of cinchomeronic acid, $C_5H_5NO_4$, a compound analogous to apophyllenic acid (compare Roser, *Annalen*, 1886, **234**, 119), and from which the *silver salt*, $C_5H_5AgNO_4$, crystallising in long, slender, colourless needles, and the *hydrochloride*, $C_5H_5NO_4 \cdot HCl$, melting with decomposition at $214-216^{\circ}$, may be formed.

Cinchomeronamide, $C_5NH_3(CONH_2)_2$, obtained in quantitative yield by the action of ammonia on diethylic cinchomerionate, is insoluble in benzene and ether, dissolves in water and ethylic alcohol, melts with evolution of gas at $163-165^{\circ}$, again solidifies, and finally melts and decomposes at 225° . With potassium hypobromite, cinchomeronamide yields both β - and γ -amidopyridinecarboxylic acids in addition to an intermediate product. The hydrochlorides of these carboxylic acids are resolved by the action of heat into β - and γ -amidopyridine respectively.

G. T. M.

Collidinepiperidine. By PETER KNUDSEN and RICHARD WOLFFENSTEIN (*Ber.*, 1895, **28**, 2275—2276).—Bromocollidine readily reacts

with piperidine to form *collidinepiperidine*, $C_{13}H_{20}N_2$, hydrogen bromide being also formed. The new base boils at $279-282^\circ$, and forms a *hydrochloride*, $C_{13}H_{20}N_2 \cdot 2HCl$. Coniine reacts in a similar manner, the corresponding derivative being formed. The *platinochloride* of *collidineconiine*, $C_{16}H_{26}N_2 \cdot 2H_2PtCl_6$, crystallises in small, red prisms, and melts and decomposes at $244-245^\circ$. The authors assume that the bromine removes the hydrogen atom combined with the nitrogen of the reduced pyridine base. A. H.

Quinoline Derivatives substituted in the Nitrogen Ring.

By ALFRED EINHORN and PENOYER SHERMAN (*Annalen*, 1895, **287**, 26—49; compare Abstr., 1891, 83).—2'-Quinolylacrylic acid is the substance employed in the preparation of those compounds described in the present paper; its *barium* salt crystallises in white needles, with $2H_2O$, the *silver* salt darkens when exposed to light, the *ethylic* salt melts at 73° , and the *amide* at $175-176^\circ$.

2'-Quinolylpropionic acid melts at $122-123^\circ$, and not at 115° as previously stated (*loc. cit.*); the *calcium* salt is anhydrous, the *platinochloride* melts and decomposes at 197° , and the *amide* melts at $149-150^\circ$.

2'-Quinolylpropylic alcohol, $C_9NH_8 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot OH$, is obtained by reducing 2'-quinolylacrylic acid with sodium amalgam in alkaline solution, or by means of tin and hydrochloric acid; it crystallises from petroleum in lustrous needles, and melts at 115° . Oxidation with potassium permanganate gives rise to 2'-quinolylpropionic acid.

2'-Quinolylglyceric acid, $C_9NH_8 \cdot CH(OH) \cdot CH(OH) \cdot COOH$, is obtained by oxidising 2'-quinolylacrylic acid with potassium permanganate; it crystallises from dilute alcohol in white leaflets which contain $3H_2O$, and in this condition melts between 100° and 150° , slowly losing water, and becoming black. The *aurochloride* crystallises in yellow prisms, and melts at 174° , the *barium* salt is anhydrous, the *ethylic* salt melts at $107-108^\circ$, and the *methylic* salt at $140-141^\circ$.

2'-Quinolylacetic acid has been already described (*loc. cit.*); the *platinochloride* is dimorphous, the *methylic* salt melts at 72° , and the *ethylic* salt at 67° .

Much evidence is adduced to show that the product of condensation between 2'-quinolylacetaldehyde and orthamidobenzaldehyde is identical with Weidel's 2'-3'-diquinolyl. M. O. F.

Hippuroflavin. By LEOPOLD RÜGHEIMER (*Annalen*, 1895, **287**, 50—97; compare Abstr., 1889, 252, and 1894, i, 55).—The author prefaces the description of his experiments with a discussion of the constitution of hippuroflavin and its derivatives; the structural formula already put forward (*loc. cit.*) continues to be adopted, and attention is drawn to the quinonic character of the substance.

Hippuroflavin (*dibenzoylisopyrazinequinone*), $C_{18}H_{10}N_2O_4$, has been already described in some detail (*loc. cit.*); the following derivatives have been prepared for the first time.

Dihydrohippuroflavindianilide (*Dianilidodihydroxydibenzoyl-nn-dihydropyrazine*), $C_{30}H_{24}N_4O_4$, is obtained by heating hippuroflavin on

the water bath with excess of aniline and glacial acetic acid; it melts and decomposes at 158—160°, and does not dissolve in common solvents, purification being effected by converting it into the *potassium* salt, which is then decomposed by the addition of water to the alcoholic solution.

When caustic soda is added in small quantities to dianilidohippuroflavin suspended in warm water, the *amidanhydride* of dibenzylamidodianilidosuccinic acid,
$$\begin{array}{c} \text{NHBz} \cdot \text{C}(\text{NHPh}) \cdot \text{C}(\text{NHPh}) \cdot \text{COOH} \\ | \qquad \qquad | \\ \text{CO} \text{ ——— } \text{NBz} \end{array}$$
, is formed;

the solid product obtained on acidifying the filtered liquid is dissolved in ammonia, and treated with calcium chloride, in order to remove the acid as *calcium* salt. The amidanhydride crystallises from alcohol in small needles, and melts with effervescence at 226—227°; the *calcium* salt forms slender, colourless needles, containing 3H₂O, and precipitates are formed when a neutral solution of the ammonium salt is treated with solutions of metallic salts.

Dihydrohippuroflavinbismethylanilide (*dimethylanilidodihydroxydibenzoyl-nn-dihydropyrazine*), C₃₂H₂₆N₄O₄, is obtained from hippuroflavin and methylaniline; it melts at 238°, previously becoming dark yellow.

Hippuroflavinbismethylanilide, C₃₂H₂₆N₄O₄, is obtained from the foregoing substance by the action of boiling nitrobenzene; it melts at 233—234°.

Dihydrohippuroflavindiorthotoluidide (*diorthotoluidobenzoyldihydroxy-nn-dihydropyrazine*), C₃₂H₂₈N₄O₄, is colourless, and melts at 235—238°, yielding orthotoluidine and *hippuroflavinorthotoluidide*, C₂₈H₁₉N₃O₄, which crystallises from benzene in stellate aggregates of needles, and melts at 208—209°.

Hippuroflavinparatoluidide, C₂₈H₁₉N₃O₄, and *hippuroflavinxylylide* melt at 246° and 223—225° respectively.

Dihydrohippuroflavindiamide (*diamidodibenzoyldihydroxy-nn-dihydropyrazine*), C₁₈H₁₆N₄O₄, is obtained by the action of ammonia on hippuroflavin; it melts at 240°, and begins to darken at 220—225°.

Hippuroflavindiamide, C₁₈H₁₄N₄O₄, is obtained by treating the foregoing compound with alcoholic ammonia in sealed tubes at 105°, for four hours; it melts at 237—238°. M. O. F.

Two new Bases in the Urine of the Insane. By MARTIN KRÜGER (*Chem. Centr.*, 1895, i, 292—293; from *Du Bois-Reymond's Arch.*, 1894, 553—555).—The one base, C₁₀H₁₃N₃O₂, is, from its resemblance to guanine, termed *epiguanine*, and crystallises from water in slender needles, and from highly dilute ammonia in silky, lustrous prisms; it dissolves in acids, in sodium carbonate solution, and in soda; from the last solvent, lustrous, broad needles are deposited, which probably consist of a sodium derivative. The *nitrate* forms polyhedral crystals; the *chromate* is deposited in lustrous prisms, the *platinochloride* in long, orange-red prisms. The *picrate* and *aurochloride* crystallise in needles. The base gives precipitates with ammonia, silver nitrate, copper sulphate, and sodium hydrogen sulphite, but not with mercuric chloride, normal, basic, or ammoniacal lead

acetate. The second base was obtained only in very small quantity from the mother liquor of epiguanine. J. B. T.

Hydrogenation of Quinine. By EDUARD LIPPMANN and FRANZ FLEISSNER (*Monatsh.*, 1895, **16**, 630—637).—When dissolved in absolute alcohol and treated with metallic sodium, quinine yields a reduction product which is apparently a tetrahydroquinine. It is an amorphous, brittle mass, which is sparingly dissolved by water, but is exceedingly soluble in alcohol, benzene, and chloroform. The base has the odour of quinoline, yields fluorescent solutions when dissolved in sulphuric acid and nitric acid, and gives the quinine reaction with ammonia and chlorine water. With a feebly acid solution, ferric chloride gives an intense green coloration, which on further addition of the reagent turns reddish-brown. These colour reactions are characteristic of the base, which also forms the following unstable salts: a *normal hydrochloride*, $C_{20}H_{28}N_2O_2 \cdot HCl + H_2O$, an *acid hydrochloride*, a *normal sulphate*, an *acid sulphate*, and a *platinochloride*, $C_{20}H_{28}N_2O_2 \cdot H_2PtCl_6$. On heating with excess of acetic anhydride, only one acetyl group enters the molecule, the compound $C_{20}H_{27}AcO_2N_2$, being formed as a viscous mass. Tetrahydroquinine therefore contains only one hydroxyl group, and from its behaviour with hydrochloric acid, whereby hydrochlorohydroapoquinine is formed, it would appear that the double linkage existing between the carbon atoms in quinine is not broken away during the addition of the four atoms of hydrogen.

Hydroquinine has a powerful toxic effect, small doses causing suspension of respiration with loss of voluntary and reflex movement, and ultimately convulsions and death. G. T. M.

Merochinine. By WILHELM KOENIGS (*Ber.*, 1895, **28**, 1986—1991).—Merochinine, which is obtained, as already described by the author (*Abstr.*, 1894, i, 392, 477), by the hydrolytic decomposition of cinchone and chinine, and by the direct oxidation of cinchonine with chromic acid, is converted into 3 : 2-methylethylpyridine by heating with hydrochloric acid and mercuric chloride at 250°. As it also contains the imido-group, it is in all probability the carboxylic acid of a hypopyridine base of the formula $C_8H_{16}N$. All attempts to convert it into the corresponding pyridinecarboxylic acid by removal of hydrogen or by elimination of hydrogen bromide from bromomerochinine have been unsuccessful, as the carboxyl group is in all cases simultaneously eliminated. When oxidised with potassium permanganate, it is converted into cincholeuonic acid, and the carboxyl group must therefore occupy the same position as one of the carboxyl groups of the latter compound.

From his researches, Skraup has concluded that in the so-called "second residue" of the cinchona alkaloids, a vinyl group is combined with one of the carbon atoms of the hypopyridine ring, and this conclusion has been supported by von Miller and Rohde (*Abstr.*, 1895, i, 435); in that case, merochinine, which is obtained from this second residue, would also contain the vinyl group, probably in combination with the 2-carbon atom of the pyridine group. The presence of this

group in cinchonine is borne out by the following results. The author and Comstock have shown (Abstr., 1887, 281) that cinchonine readily combines with 2 atoms of bromine, and on treatment with boiling alcoholic potash the product loses 2 mols. of hydrogen bromide, forming dehydrocinchonine, which must therefore either contain two ethylene linkages or an acetylene linkage. No direct proof of the presence of the latter has been obtained, but it is found that, on oxidation, one carbon atom of dehydrocinchonine is eliminated as carbonic anhydride, with formation of cinchotenine. The latter has been also obtained by Skraup by the oxidation of cinchonine; it is a saturated compound, and contains a carboxyl group, in addition to the hydroxyl group of the cinchonine, and therefore the dehydrocinchonine, from which it is prepared, cannot contain two ethylene linkages, but must contain an acetylene linkage, which is formed from the vinyl group of cinchonine by removal of hydrogen.

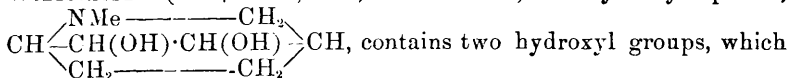
Bromomerochinine hydrobromide, $C_9NH_{14}BrO_2.HBr$, is obtained by the action of bromine water on merochinine, and is identical with the compound obtained by Comstock and Koenigs by the action of bromine water on the bye-products of the oxidation of quinine and cinchonine with chromic acid, and to which they at that time ascribed the formula $C_9NH_{13}Br_2O + \frac{1}{2}H_2O$. It forms rhombic sphenoids, melts and decomposes at $248-250^\circ$, and is reconverted into merochinine by treatment with zinc dust and sulphuric acid, all attempts, however, to convert it into a pyridine or lower hydropyridine derivative were without success.

When bromomerochinine hydrobromide is boiled with water, it readily loses one atom of bromine, and on long-continued boiling the second bromine atom is eliminated, *hydroxymerochinine*, $C_9NH_{15}O_3$, being formed. On adding ether to a solution of this compound in methylic alcohol, it crystallises out with $1H_2O$; this is evolved at 110° , the anhydrous substance melting and decomposing at 254° . The *hydrochloride*, $C_9NH_{15}O_3.HCl$, forms stellate groups of needles melting at $208-210^\circ$; the *platinochloride* small, lustrous, orange-yellow crystals melting and decomposing at 240° ; and the *aurochloride* needles melting and decomposing at 181° . The *acetyl* derivative is very soluble in water and alcohol, and yields an *aurochloride* which melts at 214° , with evolution of gas. It is only oxidised by alkaline potassium permanganate on warming, whilst merochinine and bromomerochinine are oxidised in the cold, and whereas merochinine readily undergoes etherification when hydrogen chloride is passed into its solution in methylic alcohol, the bromo- and hydroxy-derivatives can only be etherified with difficulty in this way.

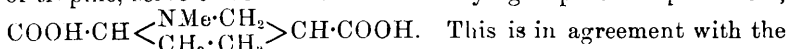
Higher brominated derivatives of merochinine may be obtained by heating bromomerochinine hydrobromide with bromine at 100° , or by the action of bromine on the hydrochloride of merochinine ethylic ether in chloroform solution. One of these is a colourless, crystalline compound melting and decomposing at 184° , and is the hydrobromide of either a tribromomerochinine, or of a monobromomerochinine dibromide.

H. G. C.

New Methods for the Preparation of Tropinic acid. By RICHARD WILLSTÄTTER (*Ber.*, 1895, 28, 2277—2280).—Dihydroxytropidine,



are united to adjacent carbon atoms; and when treated with chromic acid, it is converted into tropinic acid, identical with that obtained by the oxidation of tropine. This proves that two adjacent carbon atoms of dihydroxytropidine, and therefore also of tropine, serve to form the two carboxyl groups of tropinic acid,



above formula proposed for the acid by Merling (*Abstr.*, 1892, 358), whilst it is inconsistent with Ladenburg's formula for the same substance.

A. H.

Scopoleïnes (Ethereal Salts of Scopoline). By E. MERCK (*Chem. Centr.*, 1895, i, 434—435; from *Ber. ü. d. Jahr.*, 1894, 15—18).—The only scopoleïne found in nature is scopolamine, the scopoleïne of tropic acid, which occurs in *Scopolia japonica* and *S. atropoides*, and is identical with hyoscyne. *Acetylscopoleïne*, $\text{C}_8\text{H}_{12}\text{NO}_2\text{Ac}$, forms white crystals melting at 250° ; the *aurochloride* melts at 195 — 197° . *Benzoylscopoleïne*, $\text{C}_8\text{H}_{12}\text{NO}_2\text{Bz}$, is crystalline, and melts at 68 — 70° ; the *hydrochloride* melts and decomposes at 249 — 250° ; the *hydrobromide* crystallises in colourless prisms melting at 245 — 247° ; the *nitrate*, *platinochloride* (m. p. 200 — 201°), *aurochloride* (m. p. 188°), *mercuorchloride* (m. p. 140 — 142°), and *picrate* (m. p. 200 — 201°) have also been prepared. *Cinnamoylscopoleïne*,



slowly becomes crystalline; its *nitrate* melts at 172 — 173° ; the *hydrobromide* has also been prepared.

J. B. T.

Tropeïnes. By E. MERCK (*Chem. Centr.*, 1895, i, 434; from *Ber. ü. d. Jahr.*, 1894, 7—11).—The object of this investigation was the determination of the physiological action of the fatty acid derivatives of tropeïne. The majority have no special influence; lactyl-tropeïne exercises a well-marked effect on the heart, but it is not a mydriatic. *Acetyltropeïne*, $\text{C}_8\text{H}_4\text{NOAc}$, is a pale yellow syrup, boiling at 235 — 237° ; the *aurochloride* melts at 193° . *Lactyltropeïne*, $\text{C}_8\text{H}_4\text{NO} \cdot \text{CO} \cdot \text{CHMe} \cdot \text{OH}$, crystallises in colourless needles, and melts at 74 — 75° ; its *hydrochloride*, *hydriodide*, *nitrate*, *sulphate*, and *aurochloride* (m. p. 143 — 146°) have been prepared. *Succinyltropeïne*, $\text{C}_2\text{H}_4(\text{CO} \cdot \text{C}_8\text{H}_4\text{NO})_2$, yields a *hydrobromide* and an *aurochloride*; the former is colourless; the latter crystallises in yellow plates. The same derivatives of *malyl*-, *tartryl*-, and *hippuryl*-tropeïne have also been prepared; the *aurochlorides* melt at 203 — 204° , 233° , and 190 — 192° respectively. *Tartryltropeïne* is colourless and crystalline. *Paramethylhomotropine*, $\text{C}_8\text{H}_{14}\text{NO} \cdot \text{CO} \cdot \text{CH}(\text{OH}) \cdot \text{C}_6\text{H}_4\text{Me}$, prepared by the action of dilute hydrochloric acid on tropine paramethylmandelate, is crystalline; its *aurochloride* melts at 192 — 193° .

J. B. T.

Angostura Alkaloids. By HEINRICH BECKURTS (*Arch. Pharm.*, 1895, **233**, 410—423).—The alkaloids cusparine, cusparadine, galipine, and galipidine are obtained together from the ethereal extract of the bark of *Cusparia trifoliata*, Engler (*Galipea officinalis*, Hancock) (*Abstr.*, 1892, 642). Derivatives of cusparine only are described in the present communication. The purification of this compound from traces of galipine is extremely difficult, and is best accomplished by repeated recrystallisation from light petroleum; criteria of its purity are its melting point (89°) and the formation of colourless salts with acids. The alkaloid gives the following colour reactions. With concentrated sulphuric acid, a dull red, changing to cherry colour. Fuming nitric acid produces a yellow solution; the residue, after evaporation and treatment with potash, becomes orange. Fröhde's reagent gives a brown solution, which changes successively to violet, bluish-green, and deep blue; when warmed, the blue colour is obtained more readily, and it is produced immediately with the concentrated reagent. Sulphuric acid containing titanous anhydride and furfuraldehyde respectively gives a reddish-brown and a brownish-red solution. By the action of bromine water on cusparine hydrobromide, the *dibromide*, $C_{20}H_{19}NO_3 \cdot HBr \cdot Br_2$, is formed as a pale yellow, amorphous powder melting at 117° ; when treated with alcohol, hard yellow prismatic needles are obtained; they melt at 236° , and probably consist of *cusparine dibromide*, $C_{20}H_{19}NO_3 \cdot Br_2$. The *platinochloride* crystallises with $6H_2O$. *Cusparine methochloride*, $C_{20}H_{19}NO_3 \cdot MeCl$, prepared from the methiodide (*loc. cit.*), crystallises in lemon-coloured needles and melts at 190° . Its *platinochloride*, $(C_{20}H_{19}NO_3 \cdot Me)_2PtCl_6$, is deposited in lustrous golden needles melting at 210° ; the *aurochloride* forms reddish-brown needles and melts at 152 — 153° .

Methylcusparine, $C_{20}H_{18}NO_3 \cdot Me + \frac{1}{2}H_2O$, is prepared by the action of potash or silver oxide on cusparine methiodide; it crystallises from dilute alcohol in colourless needles, from water in pearly lustrous plates, and melts at 190° . The *hydrobromide* crystallises with $10H_2O$ in slender, lustrous, yellowish-green plates. The *hydrochloride* crystallises with $2.5H_2O$ in hard, stellate needles. The *platinochloride*, $(C_{20}H_{18}NO_3 \cdot Me)_2 \cdot H_2PtCl_6$, forms golden, lustrous needles and plates melting at 210° . The *methiodide*, $C_{20}H_{18}NO_3 \cdot Me \cdot MeI$, crystallises in slender, yellow, lustrous needles; it melts at 185° , darkens on exposure to light, and has an intensely bitter taste.

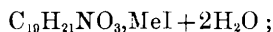
Cusparine ethiodide, $C_{20}H_{18}NO_3 \cdot EtI$, is deposited in yellow, lustrous needles, darkens when exposed to light, and melts at 201° . The *chloride* crystallises in lemon-coloured needles melting at 156° . The *platinochloride* is deposited in golden, stellate, rhombic prisms melting at 178° . *Ethylcusparine*, $C_{20}H_{18}NO_3 \cdot Et$, prepared by the action of soda on the ethiodide, crystallises in colourless, transparent prisms, and melts at 190 — 191° . The same compound, together with the *hydrate*, $C_{20}H_{18}NO_3 \cdot Et + H_2O$, is formed by the interaction of the ethiodide and silver oxide; it crystallises in lustrous plates, and melts at 114 — 115° .

J. B. T.

Alkaloids of Berberis Aquifolium. By H. POMMERHNE (*Arch. Pharm.*, 1895, **233**, 127—174).—The pulverised root of *Berberis*

aquifolium was repeatedly extracted with water containing a little acetic acid, the extract was concentrated and filtered from berberine acetate and other substances, and from the filtrate, by saturating it with sodium sulphate, oxyacanthine was eventually obtained, whilst berbamine was obtained by saturating the filtrate from the oxyacanthine with sodium nitrate. These two alkaloids were then purified by crystallisation of their hydrochlorides from water. New experiments were made with them, and some hitherto doubtful points finally decided. Some properties of berberine, as to which contradictory statements exist, were also re-examined.

Oxyacanthine.—This substance has the composition $C_{19}H_{21}NO_3$; it is a monacid base, and is identical in composition and properties with the product obtained by Hesse from *B. vulgaris*. It can be obtained as a white, amorphous precipitate, which melts at $150-160^\circ$; or, by crystallisation from 90 per cent. alcohol, in colourless crystals which melt at $208-210^\circ$. In alcoholic solution at 20° , it has the specific rotation $[\alpha]_D = +174^\circ 5'$, and it forms a well crystallised compound with lævo-, but not with dextro-, rotatory tartaric acid. It contains an hydroxyl group, for, although acetic chloride and acetic anhydride seem to exercise a dehydrating action on it, yet benzoic chloride converts it into a *monobenzoyl derivative*, of which the *platinochloride*, with $8H_2O$, and *aurochloride*, with $2H_2O$, were prepared. It probably contains 2 methoxyl groups; the numbers obtained by Zeisel's method point, curiously enough, to $1\frac{1}{2}$. It reacts as a tertiary base with *methylic iodide*, yielding an *additive compound*,



half of the water is lost at 100° , the rest at 110° ; it melts when anhydrous at $248-250^\circ$, and can be converted by means of silver oxide into an alkaline quaternary ammonium base, the *platinochloride*, with $5H_2O$, and *aurochloride*, with H_2O , of which were prepared. Oxyacanthine gives the usual alkaloid reactions. The following salts were prepared and analysed:—Hydrochloride, specific rotation $[\alpha]_D = +163^\circ 49'$, *hydrobromide*, *hydriodide* melting at $256-258^\circ$, *nitrate*, all with $2H_2O$; normal sulphate, *aurochloride*, both with $4H_2O$; *platinochloride* with $5H_2O$.

Berbamine.—This has the composition $C_{18}H_{19}NO_3$, as was shown by the analysis of its *hydrochloride*, with $2H_2O$, and *platinochloride*, with $5H_2O$. It was obtained in small quantity only, and appears to contain 1–2 methoxyl groups.

Berberine.—This alkaloid yields a normal sulphate, with $3H_2O$, in addition to the hydrogen sulphate; it also forms a stable hydrogen carbonate, $C_{26}H_{17}NO_4 \cdot H_2CO_3 + 2H_2O$, and a stable hydrocyanide. Methylic, ethylic, and amyllic iodides form additive compounds with berberine, but these quaternary ammonium derivatives are not very stable; they do not yield the corresponding chlorides when treated with silver chloride, berberine hydrochloride being formed instead.

C. F. B.

Identity of Baptitoxine and Cytisine. By PIETER C. PLUGGE (*Arch. Pharm.*, 1895, 233, 294–299).—Baptitoxine, obtained by von Schroder from the root of *Baptisia tinctoria*, is shown to be identical

with cytisine. The seeds afford a better source of the alkaloid; those of *B. australis* contain 2.85 per cent. of cytisine, and those of *B. tinctoria* probably an equal amount. C. F. B.

Estimation of Alkyl Groups attached to Nitrogen. By JOSEF HERZIG and HANS MEYER (*Monatsh.*, 1895, **16**, 599—608; compare Abstr., 1894, ii, 219; 1895, i, 310).—The authors have previously (*loc. cit.*) described a method for the detection and estimation of alkyl groups attached to nitrogen, and have shown that, by a modification of the process, the methoxyl and ethoxyl groups present can also be determined. A large number of substances have now been examined, and the results obtained in part agree with accepted constitutions, and in other cases contradict them.

The alkaloids, harmine and harmaline, each contains one methoxyl group, but no methyl attached to nitrogen (compare Fischer, Abstr., 1889, 730, and Fischer and Täuber, Abstr., 1885, 820).

Sparteïne contains no methyl group attached to nitrogen (compare Ahrens, Abstr., 1888, 611), and Ahrens' norsparteïne is only an impure form of sparteïne.

Pilocarpine contains only one methyl group attached to nitrogen and no methoxyl group, the authors therefore conclude that either Hardy and Calmel's formula, which gives three methyl groups directly attached to nitrogen must be incorrect, or that their method of estimation is unsuited to this compound.

The methyl derivative of the methylbetaine of papaverinic acid, which melts at 126°, contains four methoxyl groups (compare Schranzhofer, Abstr., 1894, i, 59 and 151). G. T. M.

Pauçine. By E. MERCK (*Chem. Centr.*, 1895, i, 434, from *Ber. ü. d. Jahr.*, 1894, 11—15).—*Pauçine*, $C_{27}H_{39}N_5O_5 + 6.5H_2O$, is the alkaloid of the "pauço nut," the fruit of *Pentaclethra macrophylla*; it crystallises in golden plates, melts at 126°, is insoluble in ether and chloroform, and a portion is decomposed when it is recrystallised from water. The *hydrochloride*, $C_{27}H_{39}N_5O_5 \cdot 2HCl + 6H_2O$, melts at 245—247°. The *platinochloride*, $C_{27}H_{39}N_5O_5 \cdot H_2PtCl_6 + 6H_2O$, is brownish-red, crystalline, and melts at 145°. The *picrate* crystallises in garnet-red prisms melting at 220°. By the action on pauçine, of potash, or of concentrated hydrochloric acid, at 150°, dimethylamine is eliminated. J. B. T.

Matrine, the Alkaloid of Sophora Angustifolia. By PIETER C. PLUGGE (*Arch. Pharm.*, 1895, **233**, 441—443).—Nagai has recently published, in Japanese, a communication on the alkaloid in the root of *Sophora angustifolia*, which he terms *matrine*, $C_{15}H_{24}N_2O$; it melts at about 80°, is, in aqueous solution, dextrogyrate, and gives precipitates, which are frequently crystalline, with the usual alkaloid reagents. The *platinochloride*, $C_{15}H_{24}N_2O \cdot H_2PtCl_6$, and the *aurochloride*, $C_{15}H_{24}N_2O \cdot HAuCl_4$, have been prepared by Nagai, and the author has obtained a crystalline *ferrocyanide*. The lethal dose of matrine is larger than that of cytisine, and the compounds differ in physiological action. J. B. T.

Organic Chemistry.

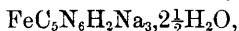
Explosive Double Salt of Potassium Cyanide and Potassium Nitrite. By KARL A. HOFMANN (*Zeit. anorg. Chem.*, 1895, 10, 259—261).—A good yield of sodium nitroferrocyanide is obtained by the action of a concentrated solution of ferrous sulphate on an aqueous solution containing equal weights of sodium nitrite and potassium cyanide. With the object of obtaining an intermediate compound, which, by the action of ferrous sulphate, is converted into the nitroferrocyanide, the author has examined the action of potassium cyanide on potassium nitrite.

When a solution of the two salts is boiled, the cyanide is converted into ammonia, and potassium carbonate, formate, and nitrate.

The *double salt*, $\text{KCN}, \text{KNO}_2 + \frac{1}{2}\text{H}_2\text{O}$, is obtained by dissolving potassium nitrite (50 grams) and potassium cyanide (20 grams) in the smallest possible quantity of water and allowing the solution to evaporate over sulphuric acid. Potassium cyanide separates first, and then the new double salt in short, characteristic prisms. It explodes with a loud report when heated at $400\text{--}500^\circ$, but does not explode on percussion; on recrystallisation in a vacuum over sulphuric acid, it is partially decomposed into its component salts. With silver nitrate, the neutral solution gives silver cyanide and silver nitrite.

E. C. R.

Sodium Nitroferrocyanide. By KARL A. HOFMANN (*Zeit. anorg. Chem.*, 1895, 10, 262—276).—*Sodium amidoferrocyanide*,



is obtained by reducing sodium nitroferrocyanide with 4 per cent. sodium amalgam, cooling the mixture with ice and salt; the product is precipitated with alcohol, re-dissolved in ice-cold water, and again precipitated. It crystallises in bright yellow needles, and its solution decomposes at the ordinary temperature yielding ammonia, ferric hydroxide, and sodium ferrocyanide. With bleaching powder and dilute sulphuric acid, it gives a beautiful reddish-violet solution; with ferrous sulphate, a bright greenish-blue precipitate; with ferric chloride, a deep blue-green precipitate; and with dilute hydrochloric acid, a green solution. When heated with sodium hydroxide, it yields ammonia, ferric hydroxide, and sodium ferrocyanide; when heated with hydroxylamine and dilute sodium hydroxide, it gives a reddish-yellow, and then a beautiful, bluish-red solution. The same compound is also obtained when a solution of sodium nitroferrocyanide, cooled with ice and salt, is treated with gaseous ammonia; the product obtained crystallised, however, with $6\text{H}_2\text{O}$. The *silver salt*, $\text{FeC}_5\text{N}_6\text{H}_2\text{Ag}_3, 3\text{H}_2\text{O}$, is obtained in white aggregates by adding silver nitrate to the aqueous solution in the presence of neutral ammonium nitrate; when treated with methyl iodide, decomposition takes place, and a residue, containing iron and cyanogen together with methyl-carbylamine, is formed. The formation of amidoferrocyanide from

nitroferrocyanide is a reduction process and not a substitution process; for amidoferrocyanide is formed by the action of mono- and diethylamine, as well as by that of ammonia. When preparing the compound by the action of these amines, hydrates, with $5\text{H}_2\text{O}$ and $7\text{H}_2\text{O}$, were obtained. When nitroferrocyanide is treated with pure trimethylamine, a brisk evolution of nitrogen takes place, and sodium ferrocyanide and ferric hydroxide are formed; when a 10 per cent. alcoholic solution of trimethylamine is employed, amidoferrocyanide is formed. Sodium amidoferrocyanide is either not altered or entirely decomposed by acetic anhydride, benzenesulphonic chloride, alcohol and carbon bisulphide or chloroform. When treated with iodine dissolved in potassium iodide or in alcohol, it gives a beautiful violet-red compound which easily decomposes into sodium ferrocyanide, ferric hydroxide, nitrogen, and ammonia. If continuously oxidised with potassium permanganate in alkaline solution at the temperature of melting ice, it yields sodium nitroferrocyanide. When treated with nitric oxide in ice-cold aqueous solution, it yields the sodium nitroferrocyanide, $\text{FeC}_5\text{N}_6\text{Na}_4\text{O}_2\text{H}_7\cdot 7\text{H}_2\text{O}$, which crystallises in yellow needles, and loses $4\frac{1}{2}$ mols. of water when allowed to remain over sulphuric acid at 50° . When the amidoferrocyanide (6 grams) is treated with sodium nitrite (1.2 grams) in ice-cold aqueous solution, and then acidified with acetic acid, a brisk evolution of gas, containing nitric oxide, takes place, and the solution turns violet-red; when this solution is made slightly alkaline and precipitated with alcohol, the compound, $(\text{Na}_3\text{FeC}_5\text{N}_6)_2\text{NONa} \cdot 16\text{H}_2\text{O}$, is obtained. It crystallises in beautiful orange-yellow needles, gives an intense violet coloration with ammonium sulphide, and does not yield ammonia when heated with sodium hydroxide. When treated with sodium nitrite and acetic acid in ice-cold solution, it is converted into sodium nitroferrocyanide. If only 0.95 gram sodium nitrite is used for 6 grams of sodium amidoferrocyanide, the compound, $(\text{Na}_3\text{FeC}_5\text{N}_6)_2\text{NH} \cdot 16\text{H}_2\text{O}$, is obtained; this crystallises in sulphur-yellow plates, gives a beautiful bluish-red solution with hydroxylamine and sodium hydroxide, a greenish-blue precipitate with ferrous chloride, an intensely blue precipitate with ferric chloride, and a violet solution with sodium nitrite and acetic acid. When heated with sodium hydroxide, it yields ammonia, and with small quantities of sodium nitrite it yields sodium nitroferrocyanide.

From the above reactions, the author points out that the amido-group in amidoferrocyanides behave in a very different manner from amido-groups in organic compounds, and he concludes that it is combined with iron as expressed in the formula $\text{NH}_2\cdot\text{Fe}(\text{CN})_5\text{Na}_3$.

E. C. R.

Action of Carbonic Anhydride, Water, and Alkalis, on Solutions of Cyanuric acid and Alkali Cyanurates. By PAUL LEMOULT (*Compt. rend.*, 1895, **121**, 404—406).—Thermochemical considerations indicate that carbonic anhydride should displace sodium from trisodium cyanurate and convert the latter into the monosodium salt, and experiment confirms this conclusion, the monosodium salt being precipitated when the gas is passed into a concentrated solution of

the trisodium salt. Further, carbonic anhydride precipitates the acid from a concentrated solution of the monosodium salt.

Direct experiment shows that, in aqueous solution, cyanuric acid is slowly converted into ammonia and carbonic anhydride. It is also found that the residue of thermal effect observed when the acid is neutralised with an alkali is much reduced if neutralisation is effected as rapidly as possible, but is greatly increased if the addition of successive equivalents of alkali is extended over several hours. These results confirm the author's view that the apparent residual heat of neutralisation is a consequence of the partial decomposition of the acid (this vol., ii, 11), this decomposition being accelerated by the presence of an alkali. C. H. B.

Bivalent Carbon: Chemistry of Cyanogen and Isocyanogen.

By JOHN U. NEF (*Annalen*, 1895, **287**, 265—359; compare Abstr., 1895, i, 3 and 9).—The author's previous investigations on the subject of bivalent carbon have dealt with aromatic and aliphatic members of the isocyanide group, which are represented by the general formula $R \cdot N \cdot C$, and with fulminic acid, which is expressed constitutionally by the formula $C \cdot NOH$. Attention is now directed towards cyanogen and isocyanogen, and regarding as possible the existence of three isomeric substances having the empirical formula C_2N_2 , namely, cyanogen, $N \cdot C \cdot C \cdot N$, cyanisocyanogen, $N \cdot C \cdot N \cdot C$, and diisocyanogen, $C \cdot N \cdot N \cdot C$ (Thiele, Abstr., 1894, i, 61), the author claims to have established by his experiments the conclusion that the cyanides are derivatives of isocyanogen, and that hydrogen cyanide itself must henceforth be looked on as hydrogen isocyanide, $HN \cdot C$. The foundation for this view is strengthened by the striking resemblance between the salts of hydroxyisocyanogen (fulminic acid) and derivatives of hydrogen isocyanide, the similarity being in some cases so close as to have given rise occasionally to confusion between the substances themselves.

If potassium cyanide is, in reality, potassium isocyanide, $KN \cdot C$, the chemical activity of an unsaturated compound will be displayed by this substance, it having been shown (Abstr., 1892, 1438) that the more positive the character of an unsaturated molecule, the more readily will additive compounds be obtained from it. It is shown by the author's investigation that potassium cyanide does actually exhibit such behaviour, forming ethylic cyanimidocarbonate when treated in dilute, aqueous solution with ethylic hypochlorite; this reaction is analogous to the conversion of isonitriles into derivatives of mesoxamide by means of carbonyl chloride (Abstr., 1892, 1438).

Ethylic cyanimidocarbonate, $C \cdot N \cdot C(NH) \cdot OEt$, is obtained by adding ethylic hypochlorite (9 grams) to a solution of potassium cyanide (18 grams) in five times the quantity of water, the liquid being constantly agitated, and maintained at a temperature of -10° . After adding about half the quantity of ethylic hypochlorite, the colourless solution becomes turbid owing to the separation of an oil, which is extracted with ether and dried with calcium chloride; on removing the solvent, an oil is obtained having a sweet, but penetrating odour, and on distilling this substance the greater part boils at

50—51° under a pressure of 30 mm., the higher fraction passing over at 80° under a pressure of 26 mm., and solidifying in the condenser. The liquid is ethylic cyanimidocarbonate, the solid being ethylic diimidoxalate, which is produced from the former compound by the action of alkali.

Ethylic cyanimidocarbonate is a colourless oil having a sweet, but penetrating odour; it is sparingly soluble in cold water, and has the sp. gr. = 1.00 at 15°. It boils at 42°, 50°, and 60°, under pressures of 20 mm., 30 mm., and 42 mm., respectively, and when distilled under atmospheric pressure, boils, and slightly decomposes at 133°. After a few days it darkens and ultimately becomes almost black, but the greater part can be recovered on distillation. Prolonged digestion on the water bath with alcoholic potash or sodium ethoxide converts the substance into potassium cyanide, alcohol, and potassium cyanate; aqueous alkalis give rise to ethylic diimidoxalate, alkali cyanide and cyanate. Ethylic cyanimidocarbonate is decomposed by hydrochloric acid into ammonium chloride and ethylic cyanocarbonate; when heated with aniline on the water bath, it yields ammonia, hydrogen cyanide, alcohol, and ammonium cyanide, whilst from the portion of the residue insoluble in cold alcohol, ethylic acetate extracts cyananiline.

Ethylic diimidoxalate, $\text{OEt}\cdot\text{C}(\text{NH})\cdot\text{C}(\text{NH})\cdot\text{OEt}$, is obtained by the action of dilute alkalis on ethylic cyanimidocarbonate; it forms heavy colourless crystals which gradually become brown; melts at 38° and has a slightly sweet, peculiar taste. The substance was obtained in an impure state by Pinner and Klein (*Ber.*, 1878, **11**, 1437), who passed cyanogen into alcoholic hydrochloric acid; their preparation was brown and melted at 25°. The pure substance boils at 69°, 80°, and 100° under pressures of 18 mm., 32 mm., and 82 mm., respectively; under atmospheric pressure it boils and slightly decomposes at 172°. It dissolves readily in water at 25°, and on cooling the liquid at 5° it solidifies to a magma of white needles consisting of a *hydrate* which contains $11\text{H}_2\text{O}$; it dissolves with difficulty in cold ether and water at 12°, calcium chloride completely removing water from the ethereal solution. Mercuric chloride produces a white, insoluble precipitate when added to aqueous ethylic diimidoxalate.

Ethylic diimidoxalate is not converted into a derivative of oxalic acid on treatment with aqueous alkalis, but on adding dilute hydrochloric acid to the salt, heat is developed, ammonium chloride and ethylic oxalate being produced; aniline at the temperature of the water bath gives rise to cyananiline.

Ethylic imidocarbonate, $\text{HN}\cdot\text{C}(\text{OEt})_2$, is obtained by adding ethylic diimidoxalate (25 grams) to an alcoholic solution of sodium ethoxide containing 4 grams of sodium, filtering from sodium cyanide which separates at 60°, and extracting with ether the diluted liquid after treatment with caustic potash; it boils at 62° and 77° under pressures of 36 mm., and 80 mm. respectively, and when distilled under atmospheric pressure, boils and slightly decomposes at 138—140°. The sp. gr. = 0.948 at 23°. Ethylic imidocarbonate has been obtained in an impure state by Sandmeyer, from potassium cyanide, caustic soda, alcohol and chlorine; it is also prepared by

gently heating ethylic cyanimidocarbonate with alcoholic sodium ethoxide. When ethylic inimidocarbonate is heated with alcoholic potash, potassium cyanate is formed; aqueous alkalis are without action on the substance.

Ethylic imidoxalate, $\text{OEt}\cdot\text{C}(\text{NH})\cdot\text{COOEt}$, is obtained by agitating a solution of ethylic diimidoxalate (48 grams) in water (240 grams) with decinormal hydrochloric acid (333 grams), and extracting the clear, neutral solution with ether; it boils at 73° under a pressure of 18 mm., and under atmospheric pressure at 175° , when it decomposes. Mercuric chloride yields a white precipitate with an aqueous solution of the substance. Very dilute hydrochloric acid converts ethylic monimidoxalate into ethylic oxalate; the hydrochloride of ethylic oxalate is formed when hydrogen chloride is passed into the solution in dry ether, and it is also obtained on submitting ethylic cyanocarbonate to the same treatment. Sodium cyanide and ethylic carbonate are produced when ethylic monimidoxalate is treated with alcoholic sodium ethoxide at -10° .

Alcoholic sodium ethoxide at -10° decomposes benzoic cyanide into ethylic benzoate and sodium cyanide, the same agent converting ethylic cyanocarbonate into hydrogen cyanide and ethylic carbonate; alcoholic hydrogen chloride, however, converts these substances into ethylic benzoylformate and ethylic imidoxalate respectively.

Ethylic cyanimidocarbonate is formed when cyanogen chloride or bromide acts on a dilute, alcoholic solution of potassium cyanide. When chlorine is led into a solution of potassium cyanide in dilute alcohol, cyanogen chloride, ethylic diimidoxalate, and ethylic cyanimidocarbonate are formed, the last named being converted by the alkali into ethylic inimidocarbonate. On adding ethylic hypochlorite to dilute alcoholic potassium cyanide at -7° , ethylic diimidoxalate is formed.

Benzeneazo-imidoformyl cyanide, $\text{NPh}\cdot\text{N}\cdot\text{C}(\text{NH})\cdot\text{C}\cdot\text{N}$, is the yellow substance obtained by Gabriel (Abstr., 1880, 41) on adding a solution of diazobenzene chloride to potassium cyanide dissolved in water, and which he regarded as having the formula $\text{NPh}\cdot\text{N}\cdot\text{C}\cdot\text{N} + \text{HCN}$ on account of the readiness with which hydrogen cyanide is eliminated; the product of this decomposition is diazobenzene cyanide, $\text{NPh}\cdot\text{N}\cdot\text{C}\cdot\text{N}$ (compare Abstr., 1895, i, 348).

Ethylic ethylimidochlorocarbonate, $\text{NEt}\cdot\text{CCl}\cdot\text{OEt}$, is obtained by adding dry ethylic hypochlorite at -5° to ethylic isocyanide at -10 to -15° , in molecular proportion, and maintaining the temperature of the mixture below 0° , it boils at 63° and 68° under pressures of 88 mm. and 100 mm. respectively, and at 126° under atmospheric pressure. The vapour has a penetrating odour resembling that of alkyl isocyanates, and vigorously attacks the eyes. Water and dilute hydrochloric acid slowly decompose ethylic ethylimidochlorocarbonate, giving rise to carbonic anhydride, ethylic chloride, diethylcarbamide, and much ethylurethane. Alcoholic sodium ethoxide converts it into *ethylic ethylimidocarbonate*, which boils at 147° , and *ethylic ethylimidocyanocarbonate* is obtained when ethylic ethylimidochlorocarbonate is added to a solution of potassium cyanide in dilute

alcohol; it is an oil which boils at 78° under a pressure of 82 mm., and has a sweet, penetrating odour.

Ethylimidochloro-formyl cyanide, $\text{NEt}\cdot\text{CCl}\cdot\text{C}\cdot\text{N}$, is obtained by allowing a mixture of cyanogen chloride and ethylic isocyanide, in molecular proportion, to remain in contact for two days, and then raising the temperature for a few minutes to 70° ; the portion distilling between 120° and 130° is agitated with very dilute hydrochloric acid, washed, dried, and redistilled. It is a colourless oil which boils at 126° , and has a penetrating odour.

Trimolecular benzoic cyanide, $[\text{COPh}\cdot\text{CN}]_3$, is obtained by heating benzoic bromide (21 grams), absolute ether (150 c.c.), and silver cyanide (20 grams) for 10 hours in a reflux apparatus from which moisture is excluded, and which is heated on a water bath at 60° . After removing the ethereal liquid, aqueous potassium cyanide is added to the residue in order to remove silver bromide, and the product is then dissolved in chloroform; it crystallises from hot benzene in pale yellow needles, and melts at 195° . The substance is insoluble in water and ether, but dissolves readily in chloroform and hot benzene; when heated at 300° , it decomposes, yielding benzonitrile. It may also be obtained from ordinary benzoic cyanide by passing hydrogen bromide into the solution in absolute ether.

Dimolecular benzoic cyanide was obtained by Wache on heating an ethereal solution of benzoic cyanide with sodium; it is also formed when benzoic chloride is agitated at -5° with a solution of potassium cyanide in dilute alcohol. It crystallises from alcohol in colourless needles, and melts at $99-100^{\circ}$ (Wache observed 95°); under a pressure of 15 mm. it boils at 220° . Ordinary benzoic cyanide is formed when benzoic anhydride and potassium cyanide in molecular proportion are heated at 190° .

When ethylic chlorocarbonate (28.5 grams) is heated with silver cyanide (36.4 grams) for six hours at $130-140^{\circ}$, a mixture of ethylic cyanocarbonate and ethylic isocyanocarbonate is formed.

Ethylic chlorocarbonate (50 grams), when agitated with a solution of potassium cyanide (32 grams) in water (96 grams) and alcohol (25 grams), cooled at -13° , yields ethylic cyanocarbonate and a small quantity of ethylic carbonate; if action proceeds at ordinary temperatures, less ethylic cyanocarbonate is formed, a substance being produced which, in the presence of water or alkalis, yields hydrogen cyanide, potassium chloride, carbonic anhydride, and alcohol.

On agitating a solution of potassium cyanide in 6 parts of water cooled at -10° or -15° whilst carbonyl chloride is slowly added, an additive compound is formed which breaks up spontaneously into hydrogen cyanide, potassium chloride, and potassium carbonate.

In 1857 Cloëz obtained from cyanogen chloride and alcoholic sodium ethoxide, an oil which he regarded as ethylic cyanate (*Compt. rend.*, **44**, 482), and this result was confirmed by Hofmann and Olshausen (*Ber.*, 1870, **3**, 269); subsequently Mulder observed that the action of cyanogen bromide on sodium ethoxide in presence of water gave rise to urethane and the substance isolated by Cloëz, which, however, has the composition $\text{OEt}\cdot\text{CN}\cdot\text{HOEt}$, and also a considerable quantity of ethylic cyanurate. Finally, Ponomareff (*Abstr.*, 1882, 937) re-

corded the formation of an oil which distilled between 90° and 200° , and had a basic odour which disappeared on heating the product in an open basin on the water bath. The author finds, in the first place, that pure cyanogen bromide is without action at 50° on sodium ethoxide suspended in absolute ether and free from alcohol; cyanogen chloride is equally inert, but if alcoholic sodium ethoxide is added to cyanogen bromide or chloride at -8° to -10° , a rise of temperature takes place, and the sole product is ethylic imidocarbonate; if the action proceeds at ordinary temperatures, the yield of ethylic imidocarbonate is diminished, urethane and ethylic cyanurate being formed in small quantity. Ethylic imidocarbonate is produced with a small quantity of urethane when excess of caustic soda or potash is added to a mixture of cyanogen chloride (or bromide), water (5 parts), and alcohol (2 parts) cooled to -5° or -10° , the temperature of the liquid being maintained below 0° ; these substances probably arise from the decomposition by water or alcohol of the intermediate product $\text{NH}\cdot\text{CCl}\cdot\text{OEt}$. When hydrogen bromide is passed into a solution of cyanogen bromide in absolute ether, a yellowish-white precipitate of imidocarbonyl bromide, $\text{NH}\cdot\text{CBr}_2$, or the hydrobromide, is formed; it is hygroscopic, and fumes in air, yielding carbonic anhydride and ammonium bromide, whilst, in a dry atmosphere, hydrogen bromide is eliminated and cyanogen bromide formed.

Phenylic imidocarbonate, $\text{NH}\cdot\text{C}(\text{OPh})_2$, is obtained by adding a solution of phenol (80 grams) and caustic potash (48.6 grams) in 300 c.c. of water to a solution of cyanogen bromide (46 grams) in 2500 c.c. of water at 20° , and crystallises from petroleum in colourless needles melting at 54° ; it is insoluble in water, but dissolves readily in organic solvents, excepting petroleum. Dilute hydrochloric acid converts it into phenylic carbonate and ammonium chloride, the action of alcoholic potash gives rise to potassium cyanate, and when heated alone in a dry tube, phenylic imidocarbonate yields phenol and phenylic cyanurate. The observation of Hofmann and Olshausen (*loc. cit.*), who passed cyanogen chloride into alcoholic sodium phenoxide and obtained phenylic cyanurate, is incorrect, neither this substance nor phenylic cyanate being formed; when an alcoholic solution of cyanogen chloride or bromide is treated with aqueous or alcoholic sodium phenoxide, phenylic imidocarbonate is the chief product, *ethylic phenylic imidocarbonate* being also formed; the latter boils at 120° under a pressure of 18 mm. The observation of Hofmann and Olshausen originates in the fact that both this salt and also phenylic imidocarbonate decompose into phenol and phenylic cyanurate when heated at 180° .

When cyanogen is passed into an ice-cold solution of potassium cyanide in dilute alcohol, ethylic cyanimidocarbonate is formed together with a small quantity of ethylic diimidoxalate; when passed into a solution of sodium ethoxide in alcohol at 0° , ethylic diimidoxalate is the sole product.

The author has devised a method of obtaining hydrogen cyanide in the pure state. The slightly abnormal vapour density of former preparations is probably due to the presence of about 2 per cent. of ammonium cyanide, and to remove this impurity, dry hydro-

gen cyanide obtained from potassium ferrocyanide and sulphuric acid is distilled from phosphoric anhydride, and the vapour, after passing through a tube maintained at $40-50^{\circ}$ containing a mixture of glass beads and phosphoric anhydride, enters a long condenser, the distillate being collected in a receiver and protected from moisture by a long tube containing calcium chloride and phosphoric anhydride. The product boils at 25° (corr.), and melts at -12° to -10° , undergoing no change when preserved for many months in closed vessels; the purest specimen previously obtained boiled at 26° (corr.), and melted at -14° (Gautier). In comparison with its salts and the alkylic isocyanides, hydrogen cyanide is a very inert substance; it does not combine with chlorine or hydrogen chloride at low temperatures, and no action takes place when it remains in contact with ethylic hypochlorite for a protracted period at -10° .

The want of harmony among the statements of previous investigators (Pinner, Abstr., 1883, 731 and 1089; and 1895, i, 264; Lengfeld and Stieglitz, Abstr., 1895, i, 277; and Claisen and Matthews, *Ber.*, 1883, 16, 311), has led the author to study the action of hydrogen chloride on hydrogen cyanide in presence of alcohol, with the result that the following observations have been made. Imidoformyl chloride, $\text{NH}\cdot\text{CHCl}$, is first formed, and unites with hydrogen cyanide forming the compound $\text{NH}\cdot\text{CH}\cdot\text{C}(\text{NH})\text{Cl}$, which takes up one or two molecular proportions of hydrogen chloride; in presence of alcohol, the product gives rise to the compound $\text{OEt}\cdot\text{CH}(\text{NH}_2)\cdot\text{CCl}(\text{NH}_2)\cdot\text{OEt}$, which is present in the mixture of salts which Pinner obtained. The intermediate compound, $\text{NH}\cdot\text{CH}\cdot\text{C}(\text{NH})\text{Cl}$, also yields ethylic diethoxyimidoglyoxylate, $\text{CH}(\text{OEt})_2\cdot\text{CCl}(\text{NH}_2)\cdot\text{OEt}$, and ethylic diethoxyorthamidoglyoxylate hydrochloride,



This brief summary is much expanded in the original paper, which contains a theoretical discussion of the results obtained.

Imidoformyl cyanide, $\text{NH}\cdot\text{CH}\cdot\text{C}\cdot\text{N}$, is prepared in the following manner. Pinner's salt, ethylformimide hydrochloride (*loc. cit.*), obtained by passing hydrogen chloride into a mixture of alcohol with a solution of hydrogen cyanide in absolute ether, is suspended in ether and treated with caustic soda; after removal of solid matter, and evaporation of the ether, an oil is deposited which is a mixture of imidoformyl cyanide, the dialcoholate, and ethylic diethoxyorthamidoglyoxylate. On distillation under reduced pressure the cyanide solidifies in the condenser. Imidoformyl cyanide melts at 87° , and boils at $120-125^{\circ}$ without decomposing; it is extremely volatile, and sublimes in closed vessels. The substance is decomposed by caustic soda or dilute hydrochloric acid, yielding ammonia and formic acid, whilst an aqueous solution quickly decomposes when heated in a sealed tube at 100° , yielding formamidine formate and ammonium formate; agitation with caustic soda and benzoic chloride gave rise to benzamide and dibenzoylformamidine. The *silver* derivative of the hydrate of imidoformyl cyanide, $\text{AgC}_2\text{N}_2\text{H}_2\cdot\text{H}_2\text{O}$, is formed on adding silver nitrate to the concentrated aqueous solution; it is crystalline and colourless, becoming black when treated with boiling water.

On heating hydrogen cyanide (10 grams) with acetic anhydride (37.4 grams) in a sealed tube for five hours at 190—200°, diacetyldicyanide is formed. When hydrogen cyanide (15 grams) remains in contact with acetic bromide (45.5 grams) for four weeks at the ordinary temperature, a hygroscopic substance is formed which decomposes on treatment with water into hydrogen cyanide, acetic acid, and hydrogen bromide; it probably consists of pyruvimide bromide, $\text{NH}:\text{CBr}\cdot\text{COME}$.

The paper concludes with a theoretical discussion of the results described. M. O. F.

Compounds of Acetone with Polyhydric Alcohols. By ARTHUR SPIER (*Ber.*, 1895, **28**, 2531—2534).—*Diacetone-erythritol*, $\text{C}_4\text{H}_6\text{O}_4(\text{C}_3\text{H}_6)_2$, prepared by Fischer's method (*Abstr.*, 1895, i, 441) from acetone and erythritol, has a bitter taste, melts at 56°, and boils at 105—106° (pressure = 29 mm.). *Diacetonearabitol*, $\text{C}_5\text{H}_8\text{O}_5(\text{C}_3\text{H}_6)_2$, is a colourless syrup with a bitter taste, and may be distilled under diminished pressure. *Diacetone-adonitol* is also a syrup which has a bitter taste, and boils at 150—155° (pressure = 17 mm.). *Diacetone-dulcitol*, $\text{C}_6\text{H}_{10}\text{O}_6(\text{C}_3\text{H}_6)_2$, crystallises in prisms, melts at 98°, and boils at 193—195° (pressure = 18 mm.). *Triacetone-sorbitol*, $\text{C}_6\text{H}_8\text{O}_6(\text{C}_3\text{H}_6)_3$, is a colourless, crystalline mass, which melts at about 40°, and boils at 170—175° (pressure = 25 mm.). *Triacetone- α -glucoheptitol*, $\text{C}_7\text{H}_{10}\text{O}_7(\text{C}_3\text{H}_6)_3$, is a thick, faintly yellow syrup, which has a bitter taste, and boils at 200—201° (pressure = 24 mm.).

Acetone is thus seen to react much more uniformly with the higher alcohols than does benzaldehyde. A. H.

Constitution of Pectins. By CHARLES F. CROSS (*Ber.*, 1895, **28**, 2609—2611).—According to Tromp de Haas and Tollens (this vol., i, 7), the atomic ratio of oxygen to hydrogen in the pectins is very nearly 1 to 2, and the percentage composition of nearly all the substances analysed is very similar to that of the oxycellulose-cellulose series. One specimen of pectin had the composition of the typical lignocellulose, jute fibre, and appears by its reactions to be a soluble lignocellulose free from the substances which usually accompany lignocellulose and react with phloroglucinol and aniline salts. The pectins appear to be distinguished from one another by differences which are quite analogous to those by means of which the various members of the group of celluloses can be distinguished.

A. H.

Preparation of Ethylamine from Aldehyde-Ammonia. By FERDINAND JEAN (*Bull. Soc. Chim.*, 1895, [3], **13**, 474; compare Cambier and Brochet, *Abstr.*, 1895, i, 641, and this vol., i, 7).—Ethylamine is readily obtained by reducing aldehyde-ammonia with zinc and hydrochloric acid by Trillat and Fayollat's method. The freshly prepared crystals (10 grams) are mixed with a little water and zinc dust (20 grams), and dilute hydrochloric acid (150 grams, 1 : 3) gradually added during 10 minutes; after the lapse of a further interval of 10 minutes, some concentrated acid (20 grams) is added, and the mixture kept cool at first, but after 45 minutes heated on a

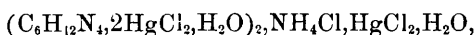
water bath; the ethylamine is then liberated by adding sufficient caustic soda to redissolve the zinc hydroxide at first precipitated, and is separated by distillation with steam.

The yield of the hydrochloride is about 30 per cent. of the aldehyde employed. As no appreciable amount of the amine is formed by the action of hydrochloric acid alone, the process seems to be purely one of reduction. JN. W.

Hexamethylenetetramine Mercurochlorides and Mercuriodide. By MARCEL DELÉPINE (*Bull. Soc. Chim.*, 1895, [3], 13, 494—497; compare *Abstr.*, 1895, i, 444).—There are three mercuriochlorides of hexamethylenetetramine. The first, $C_6H_{12}N_4 \cdot 2HgCl_2 \cdot H_2O$, obtained by exactly precipitating the aqueous amine with aqueous mercuric chloride in the cold, forms silky, white needles, and is stable at 100° , but at a higher temperature commences to decompose, finally melting at about 208° . It forms a yellowish, amorphous *additive* compound with 1 mol. of bromine at the ordinary temperature.

The second *mercuriochloride*, $C_6H_{12}N_4 \cdot HCl \cdot 2HgCl_2 \cdot H_2O$, resembles the first in appearance, and is formed in a similar manner from the hydrochloric acid solution of the amine; it melts sharply at 165° , but becomes solid again at a higher temperature, finally softening at about 210° to a yellowish-grey paste. It also forms an *additive* compound with bromine.

The third *mercuriochloride*,



is prepared by adding a concentrated solution of mercuric chloride in ammonium chloride to a boiling solution of hexamethylenetetramine containing ammonium chloride: a precipitate forms at first, but redissolves, and on cooling, the mercuriochloride separates in hard, dense, colourless prisms. It is stable at 100° , but commences to decompose at about 168° .

All three mercuriochlorides are hydrolysed by water at 100° into formaldehyde, mercuric oxide, and ammonium chloride, and the yellowish powder resulting from their decomposition at a higher temperature consists chiefly of mercuric oxide.

The *mercuriodide*, $C_6H_{12}N_4 \cdot 2HgI_2 \cdot H_2O$, is obtained by adding excess of a solution of potassium mercuriodide in dilute acetic acid to the aqueous amine; the solution is boiled until the precipitate redissolves, and the double salt separates in golden-yellow scales. It softens at 156° , and melts at 165° . JN. W.

Compounds of Amidoguanidine with the Sugars. By HEINRICH WOLFF (*Ber.*, 1895, 28, 2613—2615; compare *Abstr.*, 1894, i, 315).—*Galactoseamidoguanidine chloride* forms rhombic crystals, and is slightly dextrorotatory; *galactoseamidoguanidine sulphate* also forms rhombic crystals, which are sparingly soluble in alcohol. *Lactoseamidoguanidine sulphate* crystallises like the sulphate just described, and is dextrorotatory; the *nitrate* forms microscopic

needles, which melt and decompose at about 200° . The free bases obtained from the sulphates by means of baryta are amorphous.

A. H.

Thiamines. By FELIX LENGFELD and JULIUS STIEGLITZ (*Ber.*, 1895, **28**, 2742—2744; compare *Abstr.*, 1895, i, 264).—*Thiethylimine*, $(S:NEt)_2$, is prepared by the action of ethylamine (10 grams) dissolved in light petroleum (150 grams) on recently prepared sulphur dichloride (7.5 grams) dissolved in light petroleum (20—30 grams). The solutions must be dry, as, in presence of moisture, dark-coloured compounds are formed; the ethylamine hydrochloride is removed by filtration, and the light petroleum distilled under reduced pressure in a stream of nitrogen free from moisture, carbonic anhydride and oxygen. The thioimine is a pale-yellow, mobile oil, with an odour recalling both those of carbylamine and mercaptans; it decomposes when heated, and on standing gradually darkens. Cryoscopic molecular weight determinations agree with the above formula. The light petroleum employed was treated successively with sulphur dichloride, water, potash, dried with potassium hydroxide, and distilled, that portion boiling at 30 — 40° being employed for the experiments; unless these precautions are adopted the petroleum yields a chloro-derivative in small quantity, which cannot be removed from the thioimine.

J. B. T.

Action of Hydroxylamine Hydrochloride on Isonitrosoacetone. By MILORAD JOVITSCHITSCH (*Ber.*, 1895, **28**, 2673—2674).—A yellow, amorphous mass is obtained when isonitrosoacetone (acetone-oxime) is warmed with an aqueous solution of hydroxylamine hydrochloride; when recrystallised from water, it forms small, colourless needles, and melts and decomposes at 245 — 246° . It has the composition $C_6H_9N_3O_3$, is readily dissolved in alkalis yielding a yellow solution, and gives precipitates with solutions of most of the heavy metals. When hydrolysed with 30 per cent. sulphuric acid at 140° , it gives acetic acid, formic acid, a hydroxylamine salt, and ammonia. The substance, $C_6H_9N_3O_3$, is identical with that obtained by Scholl (*Abstr.*, 1891, 287), and the author has discontinued his investigation.

J. J. S.

$\alpha\beta$ -Trihalogen Butyric acids from the Geometrically Isomeric α -Halogen Crotonic acids. By VICTOR VALENTIN (*Ber.*, 1895, **28**, 2661—2665).—Both α -chlorocrotonic acids, when suspended in carbon bisulphide, readily absorb chlorine, and form the $\alpha\beta$ -trichlorobutyric acid previously described by Krämer and Pinner (*Ber.*, **3**, 389), Judson (*ibid.*, 785), and Garzaroli-Thurnlakh (this *Journal*, 1876, ii, 623). When warmed, the sodium salt of this acid rapidly decomposes, evolving carbonic anhydride, and giving Judson's $\alpha\alpha$ -dichloropropylene. $\alpha\beta$ -Tribromobutyric acid may be obtained in a similar manner by the addition of 2 atoms of bromine to either of the α -bromocrotonic acids (Michael and Pendleton, *Abstr.*, 1888, 1176); an aqueous solution of the sodium salt of the tribromo-acid readily evolves carbonic anhydride, and yields $\alpha\alpha$ -dibromopropylene. When the latter is heated for 12 hours at 150° with excess of alcoholic potash, it is almost entirely converted into allylene.

J. J. S.

α -Dimethylamidocaproic acid. By EDOUARD DUVILLIER (*Bull. Soc. Chim.*, 1895, [3], 13, 484—487).— α -Dimethylamidocaproic acid is formed by heating α -bromocaproic acid with aqueous dimethylamine (2 mols.) in a sealed vessel at 100° , the liberated hydrobromic acid combining with the second molecule of the amine; the product is boiled with baryta water to expel the excess of the amine, and the acid obtained by decomposing its silver salt, or better, its copper salt with hydrogen sulphide.

α -Dimethylamidocaproic acid, $\text{CH}_2\text{Pr}\cdot\text{CH}(\text{NMe}_2)\cdot\text{COOH} + 2\text{H}_2\text{O}$, crystallises in bundles of needles, and is freely soluble in water and alcohol, but insoluble in ether; when heated, it melts and sublimes, but at the same time decomposes; the melting point is not given. The *copper* salt, with $2\text{H}_2\text{O}$, crystallises in dark blue plates or scales, and melts at 110° , but neither the zinc nor the cadmium salt seems to be capable of existence. The *platinochloride* forms small, clinorhombic, orange prisms, and melts at 108° , at the same time decomposing slightly; the *aurochloride* resembles lead iodide in appearance, and a crystalline *hydrochloride* also appears to exist. JN. W.

Behaviour of the Alkali Salts of the Fatty Acids and of Soaps in presence of Water. By FRIEDRICH KRAFFT and H. WIGLOW (*Ber.*, 1895, 28, 2566—2573, 2573—2582).—III. *The Soaps as Crystalloids*.—When hot 1 per cent. aqueous solutions of sodium stearate, palmitate, myristate, laurate, elaidate, and oleate are allowed to cool, crystals begin to form respectively at 60° , 45° , 31.5° , 11° , 35° , and 0° , that is, at temperatures 9.2° , 17° , 23° , 32.6° , 16° , and 14° below the melting points of the corresponding acids. The crystals consist of a mixture of the normal and acid salts; when deposited from more dilute solutions, the crystals contain a smaller proportion of sodium, whilst from a 5 per cent. solution of sodium oleate, the neutral salt separates unchanged.

If the hot aqueous solutions are saturated with carbonic anhydride and allowed to cool, the acid salts separate out; for example, sodium hydrogen palmitate, $\text{C}_{16}\text{H}_{31}\text{O}_2\text{Na}$, $\text{C}_{16}\text{H}_{32}\text{O}_2$. The temperature at which any one of these separates lies above the melting point of the corresponding acid, but below that of the sodium hydrogen salt.

IV. *The Soaps as Colloids*.—The soaps have been examined with respect to the extent to which they raise the boiling point of water in Beckmann's apparatus. Sodium acetate and propionate act as if each molecule were dissociated into two; but, curiously enough the molecular weight, as calculated from the observed rise of the boiling point, does not increase with increasing concentration, but actually diminishes. With sodium caproate, a slight increase is observed; but in very strong solutions the thermometer actually begins to sink again, and the solution solidifies, on cooling, to a gelatinous mass. Sodium nonylate and laurate are comparatively little dissociated in moderately dilute solutions, and their molecular weights increase with increasing concentration to about double the theoretical. Sodium palmitate, stearate, and oleate at first produce a rise in the boiling point, but eventually, as the solutions become more concentrated, the thermometer falls to the boiling point of the

water used, and the solutions solidify on cooling to gelatinous masses. The soaps, then, under these circumstances, do not raise the boiling point of water in which they are dissolved, and, so far, exhibit the behaviour of colloïd substances such as gelatin and starch.

C. F. B.

Derivatives of β -Chlorocrotonic acid. By WL. SZENIC and R. TAGGESELL (*Ber.*, 1895, **28**, 2665—2672).—Both Geuther's β -chlorocrotonic acids (*Zeit. für Chemie*, 1871, 240), when dissolved in carbon bisulphide, readily absorb chlorine, and yield $\alpha\beta$ -trichlorobutyric acid, which crystallises in rhombic plates, and melts at 51.5 — 52° . It is only sparingly soluble in water, but readily in alcohol, ether, benzene, &c. If an aqueous solution of the trichlorinated acid is treated with granulated zinc and left for several weeks, a mixture of the zinc salts of β -chloroisocrotonic acid and β -chlorocrotonic acid is formed. A solution of sodium trichlorobutyrate, when heated at 100° , evolves carbonic anhydride and yields $\alpha\beta$ -dichloropropylene; the latter readily absorbs chlorine, and yields a tetrachloropropane which is identical with that obtained by Borsche and Fittig (*Annalen*, **133**, 114) by the action of phosphorus pentachloride on unsymmetrical dichloroacetone. By treating the $\alpha\beta$ -trichlorobutyric acid with alcoholic potash, a mixture of two isomeric dichlorocrotonic acids is obtained; the one which is formed in larger quantity melts at 75.5° , and is the centric symmetrical $\alpha\beta$ -dichlorocrotonic acid. The one formed in smaller quantity melts at 92° , and is identical with the $\alpha\beta$ -dichlorocrotonic acid obtained by the addition of two atoms of chlorine to tetrolic acid; it must, therefore, be the plane symmetrical isomeride. The acid melting at 92° is readily converted into tetrolic acid when treated with zinc, whereas the acid melting at 75° is not.

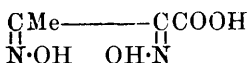
J. J. S.

Action of Hydroxylamine Hydrochloride on Ethylic Isonitrosoacetoacetate. By MILORAD JOVITSCHITSCH (*Ber.*, 1895, **28**, 2675—2683).—By warming ethylic isonitrosoacetoacetate with hydroxylamine hydrochloride, the author has obtained a substance which crystallises in colourless, glistening plates, turns red at 120° , and is completely decomposed at 141 — 142° ; it is readily soluble in ether and in alcohol, sparingly in water, and quite insoluble in light petroleum. It dissolves in alkalis, yielding a deep red solution, but is decomposed when boiled with excess of potassium hydroxide, yielding hydrogen cyanide and the substance $C_6H_9N_3O_3$, this vol., i, 79. Aqueous sulphuric acid also decomposes the compound, yielding hydroxylamine and the compound $C_6H_9N_3O_3$. The author terms the substance *oximidomethylisoxazolone*, $\begin{matrix} \text{N:CMe} \\ \text{O} \end{matrix} > \text{C:N-OH}$, and

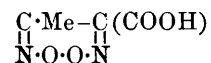
thinks it is identical with the substance previously described by Ceresole and Koeckert (*Abstr.*, 1884, 1120) and by Nussberger (*Abstr.*, 1892, 1175). The silver derivative is obtained as a red, crystalline precipitate on the addition of silver nitrate to the solution of the oxazolone or of its salts. The red precipitate usually contains

more or less of a colourless silver salt mixed with it; this colourless salt is more readily soluble in nitric acid than the red one, and the two may be separated by this means. The red salt is explosive, especially when previously heated for some time at 100° . The colourless salt is *silver normal diisonitrosobutyrate*; it readily explodes, and also turns black when heated with water. When warmed with an alkali carbonate, the oximidomethylisoxazolone is rapidly converted into diisonitrosobutyric acid, the silver salt of which, when oxidised with nitric acid (sp. gr. 1.3), yields the peroxide of diisonitrosobutyric acid previously described by Angeli (Abstr., 1893, i, 310). The *silver salt* crystallises in colourless plates, and is explosive; the *ethylic salt* may be obtained by oxidising ethylic diisonitrosobutyrate with nitric acid; it is a thick, oily substance which boils at $240-242^{\circ}$. When silver oximidomethylisoxazolone is oxidised with nitric acid, a small quantity of Angeli's acid is obtained, together with the silver salt of an isomeric acid. This *silver salt* crystallises from water in silky needles. The corresponding acid, $C_4H_4N_2O_4$, differs from Angeli's acid in being only sparingly soluble in ether, in containing no water of crystallisation, and in the sweet taste of its sodium salt.

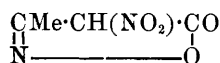
The following formulæ are given for the various acids:—



Syn-diisonitrosobutyric acid.



Angeli's peroxide acid.



Nitromethylisoxazolone.

J. J. S.

Preparation of Ethylic Isonitrosoacetoacetate and of an Isomeride from Ethylic Acetoacetate.

By MILORAD JOVITSCHITSCH (*Ber.*, 1895, 28, 2683—2687; compare Abstr., 1878, 396; 1882, 949 and 1052).—The author recommends the following method for the preparation of ethylic isonitrosoacetoacetate. Sodium nitrite (1 mol.) is intimately mixed with ethylic acetoacetate (1 mol.), and to the well-cooled mixture 18 per cent. sulphuric acid ($\frac{1}{2}$ mol.) is slowly run in; after dilution with water, the solution is extracted with ether, the ether evaporated, and the residue dissolved in light petroleum, this solution is then dried with anhydrous sodium sulphate, and, on evaporation, gives a 90 per cent. yield of the isonitroso-compound. When oxidised with nitric acid containing nitrous acid, it yields ethylic oximidonitroacetate (Abstr., 1895, i, 447), which can also be obtained in small quantities directly from ethylic acetoacetate by the action of nitric acid (sp. gr. 1.4) and a small quantity of sodium nitrite in the cold. The chief product of this action, however, is the compound $\text{O} \cdot \text{N} \cdot \text{C} \cdot \text{COOEt}$ (Cramer, Abstr., 1892, 699), which the author terms *ethylic peroxydiisonitrososuccinate*. If, in the above reaction, an excess of sodium nitrite is used, the product formed is a yellow oil, which does not crystallise and has the same percentage composition as ethylic isonitrosoacetoacetate. It differs from its isomeride in the ease with which it is decomposed by dilute alkali, yielding a yellow solution. With hydroxylamine hydrochloride, it yields oximidomethyl-

isoxazolone; on oxidation, it gives the same products as ethylic isonitrosoacetate, and, with phenylhydrazine hydrochloride, it yields 4-oximido-3:1-methylphenylpyrazolone. The new isomeride can also be prepared by the action of nitrous acid on ordinary ethylic isonitrosoacetate.

The author considers the two compounds as *syn*- and *anti*-isomerides according to Hantzsch's terminology. The new compound is ethylic *syn*-isonitrosoacetoacetate, and the old compound is the *anti*-isomeride. When treated with bromine (1 mol.), the two compounds yield the corresponding monobromo-derivatives; these are both oils, but differ in their action with alkalis. J. J. S.

Preparation of the Oxime of Ethylic Acetoacetate and its Derivatives. By ROBERT SCHIFF (*Ber.*, 1895, **28**, 2731—2734).—

Ethylic acetoacetate and aniline are dissolved at the ordinary temperature in concentrated aqueous solution of hydroxylamine hydrochloride (all in molecular proportion); when cool, the solution is extracted with ether, and on evaporating the latter the *oxime* remains as a reddish oil, which slowly changes into a crystalline condensation product melting at 124.5—125°. If, instead of extracting with ether, the solution is saturated with sodium carbonate, acetoacetic anilide oxime, $\text{NOH}:\text{CMe}:\text{CH}_2:\text{CO}\cdot\text{NHPh}$, is formed; it has been recently prepared by Knorr and Reuter (*Abstr.*, 1894, i, 371). Ethylic

acetoacetate amphidioxime, $\begin{array}{c} \text{CMe}-\text{C}\cdot\text{COOEt} \\ \parallel \quad \parallel \\ \text{N}\cdot\text{OH} \quad \text{N}\cdot\text{OH} \end{array}$, is obtained by the action

of sulphuric acid (30 per cent.) and sodium nitrite on the monoxime; contrary to the statement of Nussberger, it gives, with cupric acetate, a brown coloration and then a brown precipitate.

Ketomethylisoxazolone phenylhydrazone, $\begin{array}{c} \text{CMe:N} \\ \text{NHPh:N:C} \end{array} > \text{O}$, is prepared by treating the solution of ethylic acetoacetate, aniline, and hydroxylamine hydrochloride, as above, with hydrochloric acid and sodium nitrite (compare Knorr and Reuter, *loc. cit.*). *Benzylidene-*

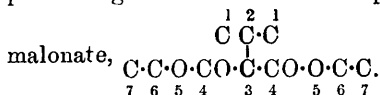
ketomethylisoxazolone, $\begin{array}{c} \text{CMe:N} \\ \text{CHPh:C} \end{array} > \text{O}$, is obtained by any of the

following methods: (1) simple mixing of the oxime and benzaldehyde, (2) saturation of an ethereal solution of the oxime and aldehyde with hydrogen chloride, (3) addition of concentrated hydrochloric acid to a mixture of the oxime and aldehyde, (4) addition of fuming hydrochloric acid to a mixture of the aldehyde and acetoacetic anilide oxime. The first method is the least, the third generally the most, satisfactory. The compound, which is deposited in pale yellow, lustrous crystals, softens at 139°, melts and in part decomposes at 141°, and is extremely stable towards acids, being precipitated unchanged from concentrated sulphuric acid on dilution. It is readily soluble in sodium carbonate solution, in potash, and in ammonia, and, if the solution has not been unduly heated, it is reprecipitated on the addition of an acid; if boiled with ammonia for a short time, however, the compound is completely decomposed, benzaldehyde being regenerated. Its solubility in alkalis suggests that in their presence the

isoxazolone ring is resolved, the acid $\text{NOH}:\text{CMe}:\text{C}(\text{CHPh})\cdot\text{COOH}$ being formed. J. B. T.

Crystallised Lactic acid of Constant Boiling Point. By FRIEDRICH KRAFFT and W. A. DYES (*Ber.*, 1895, **28**, 2589—2597).—This may be obtained by drying the commercial acid—best of sp. gr. 1.16—for a week or two in a (? vacuum) desiccator, and distilling it twice under a pressure of 12.15 mm., obtained by means of the water pump. The distillation flask should have a capacity of 60—80 c.c., and should not be more than half filled; the side tube should be wide and as low in the neck as possible, and the receiver should be kept at a temperature of 90—100° to prevent the condensation of water in it; the liquid is first heated in a water bath at 70° to drive off water, and then the residual acid is distilled as rapidly as possible, being heated by a small, rather smoky flame kept in motion under the flask. The product obtained in this way contains 99—99.5 per cent. of the acid; it boils at about 122° under 14—15 mm., at 119—120° under 13—14 mm., and at 82—85° under 0.5—1 mm. pressure; when cooled, it solidifies to white crystals which melt at about 18°, and it is very hygroscopic. C. F. B.

Formation of Carbon Chains: Alkylation of Ethylic Malonate and Acetoacetate. By CARL A. BISCHOFF (*Ber.*, 1895, **28**, 2616—2631).—The velocity of formation of the alkyl derivatives of ethylic malonate and acetoacetate cannot be deduced simply from the time which elapses before the reacting mixture of ethereal salt, sodium ethoxide, and alkyl iodide, or bromide assumes a neutral reaction, because several other reactions may occur which also lead to a condition of neutrality. Thus, the following may all take place: (1) hydrolysis of the original ethereal salt, (2) hydrolysis of the ethereal salt produced, (3) production of an ether of the alkyl group, (4) elimination of the halogen combined with hydrogen, (5) exchange of the alkyl group of the ethereal salt with that of the iodide added. It is therefore necessary to determine experimentally in each case the amount of the "normal" product obtained. For the purposes of comparison, the author numbers the chain of atoms of the normal product in order, beginning with that carbon atom of the alkyl group which is most remote from the methylene group of the original ethereal salt, and proceeding as shown in the accompanying scheme for ethylic isopropyl-



The course of the reaction is found to depend on the presence of carbon atoms at the positions 1—5 and 1—6; the more carbon atoms there are in these positions, the less readily does the "normal" reaction proceed. In many cases, moreover, the iodide reacts more readily than the bromide. These results are in agreement with the author's "dynamical theory."

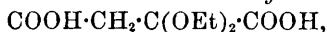
The following are the experimental details. *Derivatives of ethylic malonate*; the numbers express the percentage of the theoretical

amount which is experimentally obtained. Methyl-, 70—80 per cent., propyl-, 61—75 per cent.; the bromide gives the better yield; ethyl-, 73—80 per cent.; isopropyl-, 77—85 per cent.; butyl-, about 20 per cent.; isobutyl-, 20—40 per cent.; pseudobutyl-, the "normal" product was not formed either from the chloride or iodide under the usual conditions; traces were produced under a pressure of 5 atmos.; isoamyl-, about 25 per cent.; tertiary amyl-, the "normal" product, was only formed in very small quantity; allyl- good yield. Methylic malonate gives a yield of 75 per cent. of the methylic derivative.

Derivatives of ethylic acetoacetate: Methyl-, 76 per cent. from the iodide, 46 per cent. from the bromide; ethyl-, 60 per cent.; propyl-, 72—78 per cent.; isopropyl-, the "normal" product is readily formed from the iodide, but only in traces from the bromide; isobutyl-, 66 per cent. from the iodide, only 6 per cent. from the bromide; pseudobutyl-, the normal reaction does not occur when the chloride is used; isoamyl-, 75 per cent.; tertiary amyl-, the normal reaction does not occur; allyl-, 53—54 per cent. A. H.

Action of Acetic Anhydride on the Acids of the Acetylene Series. By ARTHUR MICHAEL and JOHN E. BUCHER (*Ber.*, 1895, 28, 2511—2512).—Acetylenedicarboxylic acid is converted by acetic

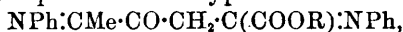
anhydride at 100° into *acetoxymaleic anhydride*, $\text{OAc} \cdot \text{C} \begin{smallmatrix} \text{CO} \cdot \text{O} \\ \text{CH} \cdot \text{CO} \end{smallmatrix}$, which melts at 89—91°; alcohol converts this into ethylic acetate and oxalacetate, whilst cold water produces the corresponding acids. When ethylic dibromosuccinate, melting at 58°, is treated with sodium ethoxide, the product consists of about 80 per cent. of ethylic *as*-diethoxysuccinate, and 20 per cent. of ethylic ethoxymaleate or ethoxyfumarate. Both of these ethereal salts are converted by hydrolysis into the sodium salt of a *diethoxysuccinic acid*,



which loses the elements of ether when heated at 100° or allowed to stand in a vacuum for some time, oxalacetic acid being formed. The same intermediate product is formed when Nef's ethylic ethoxyfumarate (*Abstr.*, 1893, i, 628) is heated with alcoholic soda.

Phenylpropionic acid is converted by acetic anhydride into a substance melting at 253°, which has the formula of phenylpropionic anhydride, but is probably the anhydride of a polymeric dibasic acid. On reduction, this substance is converted into an acid which has the composition of the truxillic acids, but is not identical with any of the acids described by Liebermann. A. H.

Action of Primary Aromatic Amines on Unsymmetrical Ketonic Compounds. By LOUIS SIMON (*Bull. Soc. Chim.*, 1895, (3), 13, 474—484; compare *Abstr.*, 1894, i, 509).—The present instalment of the paper deals with the action of aniline on the alkylic pyruvates, including the ethylic, active amylic, isoamylic, allylic, and benzylic salts; all these substances combine with aniline to form compounds of the type



probably by condensation of two molecules of the alkylic anilido-pyruvate, in a manner analogous to the condensation of aldehyde-aniline observed by von Miller and Plöchl.

Ethylic pyruvate is readily prepared by boiling the acid with alcohol in a reflux apparatus under ordinary pressure, and fractionating the product under low pressure; the yield is 90 per cent. of that indicated by theory, and the product particularly pure. Ethylic pyruvate is an almost colourless liquid, resembling ethylic acetate in odour, and boiling at 66° (18—20 mm.), and at 155° under the ordinary pressure, in the latter case decomposing slightly; the sp. gr. = 1.080 at 14° ; it is freely soluble in water, rapidly becoming hydrolysed into its proximate constituents. The hydrazone is identical with that prepared by Fischer from the hydrazone of pyruvic acid.

The product of the condensation of ethylic pyruvate with aniline, $C_{20}H_{20}N_2O_3$, the molecular weight of which was determined by the cryoscopic method, is a white, crystalline solid, melting at 146° ; it appears to form two products with phenylhydrazine, a white substance melting at 55° , and a yellowish-white substance melting at 119 — 120° . Besides the more complex condensation product, some aniluvitonic acid (methylquinolinecarboxylic acid) is formed at the same time.

Ethylic pyruvate condenses with paratoluidine in a similar manner, a substance, $C_{22}H_{24}N_2O_3$, being formed, which crystallises in colourless needles and melts at 186° ; at the same time, a second white crystalline substance, melting at 140 — 143° , is produced.

The condensation product of aniline with active amylic pyruvate melts at 110 — 111° , and is unaccompanied by any other product.

Isoamylic pyruvate is prepared in the same way as the ethylic salt; it is a limpid, yellowish liquid, having an odour resembling that of amylic acetate, and boiling at 86° (14 mm.), and at about 185° under the ordinary pressure; sp. gr. = 0.978 at 18° . The phenylhydrazone, which is very soluble in ether, melts at about 185 — 186° . The product of the condensation of isoamylic pyruvate with aniline, $C_{23}H_{26}N_2O_3$, crystallises in well-defined needles, and melts at 126 — 127° . The condensation product with paratoluidine, $C_{25}H_{30}N_2O_3$, melts at 140° .

Allylic pyruvate is prepared by passing hydrogen chloride into a mixture of the acid and the alcohol; it is a colourless liquid, having a pungent odour, and boiling at 65° (14 mm.), and at 165° under the ordinary pressure; sp. gr. = 1.082 at 17.5° . It unites with phenylhydrazine to form a yellow product melting at 185° , which does not appear to be the hydrazone. The condensation product with aniline, $C_{24}H_{26}N_2O_3$, melts at 136° .

Benzylic pyruvate is prepared directly from its proximate constituents; it is a liquid boiling at 103 — 104° (26 mm.), 107 — 108° (36 mm.), and at 207 — 208° under the ordinary pressure; sp. gr. = 1.090 at 14° . The phenylhydrazone is a yellow substance melting at 150° . The condensation product with aniline, $C_{22}H_{22}N_2O_3$, melts at 173 — 174° ; if kept, however, in the liquid in which it is formed, it is converted into a substance having a higher melting point and containing relatively more carbon.

In the preparation of benzylic pyruvate, a liquid is obtained, which, although closely resembling it, forms a compound with phenylhydra-

zine containing a much larger percentage of carbon than the hydrazone of the benzylic salt. JN. W.

Constitution of Tetric (α -Methyltetronic) acid. By LUDWIG WOLFF (*Annalen*, 1895, **288**, 1—37; compare Abstr., 1893, i, 689).—The author discusses the structure of tetric acid, which he regards as having the constitution attributed to it by Michael, $\begin{array}{c} \text{CO} - \text{CH}_2 \\ | \\ \text{CHMe} \cdot \text{CO} \end{array} > \text{O}$; it is proposed to substitute the name α -methyltetronic acid for tetric acid, it being a methyl derivative of tetronic acid, $\begin{array}{c} \text{CO} \cdot \text{CH}_2 \\ | \\ \text{CH}_2 \cdot \text{CO} \end{array} > \text{O}$, a substance which will be described in a future communication. Pentic acid, therefore, will be called α -ethyltetronic acid.

α -Methyltetronic acid (Demarçay, Abstr., 1880, 625) is obtained by brominating ethylic methylacetoacetate and heating the product for two hours at 120° ; when heated with an aqueous solution of barium hydroxide for 30 hours in a reflux apparatus, it yields glycollic and propionic acids, ethylketole being formed at the same time.

Ethylketole, $\text{C}_2\text{H}_5 \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{OH}$, is obtained by heating α -methyltetronic acid (10 grams) with water (60 grams) in a sealed tube at 200 — 210° ; it is a neutral, colourless oil which boils at 155 — 156° , and decomposes slightly under a pressure of 741 mm. It is readily soluble in water, alcohol, and ether, being precipitated from the aqueous solution by salts; the substance reduces Fehling's solution and a silver solution, and is slowly decomposed by alkalis. The *phenylhydrazone* crystallises from petroleum in yellowish prisms, and melts at 76 — 77° ; the *osazone* crystallises in lustrous, yellow prisms, and melts at 116° . Carbonic anhydride and propionic acid are obtained on oxidising α -methyltetronic acid.

The *anilide* of α -methyltetronic acid, $\begin{array}{c} \text{NHPh} \cdot \text{CH} - \text{CH}_2 \\ | \\ \text{CHMe} \cdot \text{CO} \end{array} > \text{O}$, is obtained by treating the acid with boiling aniline, and pouring the product into water; it crystallises in small, slender needles, and is resolved into its components by boiling, dilute hydrochloric acid. Its *nitroso*-derivative crystallises in yellow needles, and melts and evolves gas at 103 — 104° .

α -Methyl- β -anilidobutyrolactone, $\begin{array}{c} \text{NHPh} \cdot \text{CH} - \text{CH}_2 \\ | \\ \text{CHMe} \cdot \text{CO} \end{array} > \text{O}$, is formed when the anilide is reduced with sodium and amyl alcohol; it crystallises from hot water in long needles, and melts at 92° . The aqueous solution is neutral, and indifferent towards boiling dilute hydrochloric acid; Fehling's solution is reduced by it when heated. The *barium* salt of the hydroxy-acid is obtained on treating the lactone with boiling aqueous barium hydroxide.

The author has obtained the bromo-derivative of α -methyltetronic acid in long needles which sinter at 85° and melt at 87 — 88° ; the bromotetric acid prepared by Moscheles and Cornelius melted at 75° . The aqueous solution is feebly acid, and after some time contains hydrobromic acid; when heated at 100° , it yields carbonic anhydride, diacetyl, and methyltetronic acid, a pungent oil which probably con-

sists of bromomethylketole being formed at the same time. Bromomethyltetronic acid is immediately dissolved by ammonia and alkalis, and slowly by alkali carbonates, the bromide of the metal being formed; a concentrated aqueous solution of sodium carbonate gives rise to methyltetronic acid and diacetyl.

Methyltetronic acid is readily oxidised, yielding diacetyl, carbonic anhydride, formic and propionic acids, and an oil which closely resembles ethylketole.

Nitroso- α -methyltetronic acid, $\text{NO} \cdot \text{C} \begin{smallmatrix} \text{CO}-\text{CH}_2 \\ | \\ \text{CMe} \end{smallmatrix} \cdot \text{CO} > \text{O}$, is obtained by suspending α -methyltetronic acid in glacial acetic acid, cooling the liquid with ice, and submitting it to the action of a current of gas obtained from arsenious anhydride and nitric acid. On adding water to its solution in acetone, it crystallises out in minute prisms, and melts, evolving gas, at $130-131^\circ$; it is indifferent towards cold water and hydrochloric acid, but yields nitrous acid and methyltetronic acid with a small quantity of α -oximidopropionic acid when treated with the boiling agents. Cold aqueous ammonia gives rise to ammonium nitrite, methyltetronic acid, α -oximidopropionamide, and glycollic acid.

α -Oximidopropionylglycollic acid, $\text{NOH} \cdot \text{CMe} \cdot \text{CO} \cdot \text{O} \cdot \text{CH}_2 \cdot \text{COOH}$, is obtained when the gas from nitric acid and arsenious anhydride acts on methyltetronic acid in presence of water, and it is prepared in the form of the sodium salt by dissolving the original substance in concentrated aqueous sodium nitrite. It crystallises from water in large, transparent prisms, and undergoes no change at 100° ; it melts at 165° , slowly evolving gas, and is occasionally obtained in the form of needles containing water, which effloresce on exposure to air. The *sodium* salt crystallises in lustrous needles containing $1\text{H}_2\text{O}$; the *silver* salt crystallises in needles which soon become prisms. The *acetyl* derivative crystallises from benzene; it sinters at 102° , and melts at 105° . Cold caustic soda, hydrochloric acid, and boiling water decompose α -oximidopropionylglycollic acid, giving rise to α -oximidopropionic acid and glycollic acid; the amide of the former acid is produced by the action of ammonia, glycollic acid being formed at the same time. α -Oximidopropionylglycollic acid is obtained from nitrosomethyltartronic acid by treating it with boiling solutions of sodium nitrite and sodium acetate, which, however, are without action when cold. The *anhydride*, which may have the constitution $\text{N} \leq \text{O} \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{CMe} - \text{CO} > \text{O}$, is obtained as a bye-product in preparing the acid from α -methyltetronic acid by means of sodium nitrite; it is an amorphous, hygroscopic powder, which begins to decompose at 70° , evolving gas vigorously at 150° . It dissolves readily in alkalis and concentrated acids, and is converted into α -oximidopropionylglycollic acid on treatment with boiling water. M. O. F.

Dimethylvioluric acid and Dimethyldilituric acid. By RUDOLF ANDREASCH (*Monatsh.*, **16**, 773—788; compare *Abstr.*, 1895, i, 336).—When dimethylvioluric acid is heated in a water bath with excess of potash, and the product acidified with acetic acid, carbonic anhydride, methylamine, and oximidomalonic acid are formed. If

barium hydroxide solution be substituted for the potash, carbonic anhydride and *oximidodimethylmalonamide*, $\text{HO}\cdot\text{N}\cdot\text{C}(\text{CO}\cdot\text{NHMe})_2$, are obtained. The latter crystallises from water and from alcohol in needles, and melts at 228° (uncorr.).

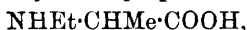
Nitrodimethylbarbituric acid, if boiled with baryta water, or allowed to remain in contact with potash for several days, yields *nitrodimethylmalonamide*, $\text{NO}_2\cdot\text{CH}(\text{COOH})_2$, which crystallises from hot water in needles, melts at 156° (uncorr.), and yields a *barium salt*, $(\text{C}_5\text{H}_8\text{N}_3\text{O}_4)_2\text{Ba} + \text{H}_2\text{O}$, which crystallises in drusy masses of prisms, a *potassium salt*, which crystallises in white needles, and a *copper salt*, which is soluble in water, and crystallises in sky-blue octahedra. Nitrodimethylmalonamide, when heated with hydrochloric acid in sealed tubes at 110° , yields formic acid, carbonic anhydride, hydroxylamine, and methylamine. An aqueous solution is converted by chlorine and bromine into *chloronitrodimethylmalonamide* and *bromonitrodimethylmalonamide* respectively; the former crystallises in spear shaped needles and melts at 109° (uncorr.), the latter forms four-sided plates and melts at $137\text{--}138^\circ$ (uncorr.). These compounds do not yield salts, the halogen having become attached to the carbon atom bearing the nitro-group. Nitrodimethylbarbituric acid forms similarly constituted compounds when treated with chlorine water and bromine water respectively. *Chloronitrodimethylbarbituric acid*,



thus obtained, crystallises from chloroform in slender needles, and from alcohol in octahedra, and decomposes at 150° . *Bromonitrodimethylbarbituric acid*, $\text{C}_6\text{H}_6\text{BrN}_3\text{O}_5$, closely resembles the corresponding chloro-compound, turns yellow at 149° , and melts partially at 152° .

G. T. M.

Methylethylhydantoïn (Ethylpropiohydantoïn). By EDOUARD DUVILLIER (*Bull. Soc. Chim.*, 1895, [3], 13, 487—490).—When carbamide is heated with α -ethylamidopropionic acid,



methylethylhydantoïn (ethylactylcarbamide), $\begin{matrix} \text{CHMe}\cdot\text{NEt} \\ \text{CO}\text{---}\text{NH} \end{matrix} > \text{CO}$, is formed, the hydantoic acid appearing to condense at once to the lactam.

Methylethylhydantoïn crystallises in transparent, rhomboidal plates, and is very deliquescent; it is stable towards boiling baryta water, so that the corresponding hydantoic acid cannot be formed by the action of this agent; the lactam is also formed instead of the acid by the action of potassium cyanate on ethylamidopropionic acid.

It thus appears that this hydantoic acid is as unstable as the corresponding creatine, a ring compound being formed in both cases where an open chain compound might be expected. JN. W.

Thiohydantoïn. By RUDOLF ANDREASCH (*Monatsh.*, 1895, 16, 789—797; compare *Abstr.*, 1888, 47).—*Thiohydantoïnacetic acid*, $\text{COOH}\cdot\text{CH}_2 < \begin{matrix} \text{CH}\text{---}\text{S} \\ \text{CO}\cdot\text{NH} \end{matrix} > \text{C}\cdot\text{NH}$, is obtained on heating together at 105° , a mixture of maleïc or fumaric acid (5 grams), thiocarbamide (3.3

grams), and water (4 c.c.). It is sparingly soluble in cold water, does not dissolve in alcohol, and has a powerful acid reaction (compare Tambach, Abstr., 1895, i, 13). When boiled with barium hydroxide, the acid is resolved into thiomalic acid, and probably cyanamide, although this was not identified, since from these two substances thiohydantoïnacetic acid can be directly synthesised. On oxidation with barium chlorate in hydrochloric acid solution, thiohydantoïnacetic acid yields carbamide and hydrothiosuccinic acid,



Diphenylthiohydantoïnacetic acid, obtained on heating a mixture of diphenylthiocarbamide and maleïc acid for $1\frac{1}{2}$ —2 hours at 140 — 144° , crystallises from alcohol in yellowish, nodular masses, and melts at 188° (compare Tambach, *loc. cit.*). G. T. M.

Formation of 1 : 3 : 5-Trinitrobenzene and 1 : 4-Nitrophenol from Nitromalonic Aldehyde. By HENRY B. HILL and JOSEPH TORRAY (*Ber.*, 1895, **28**, 2597—2599).—The sodium derivative of nitromalonic aldehyde, $\text{NO}_2 \cdot \text{CNa}(\text{CHO})_2$, is formed when sodium nitrite acts on mucobromic acid. When its aqueous solution is treated with an equivalent quantity of hydrochloric acid and warmed, or simply allowed to remain, 1 : 3 : 5-trinitrobenzene and formic acid are formed. If its aqueous solution is treated with acetone (1 mol.), and soda is gradually added, 1 : 4-nitrophenol is formed. C. F. B.

Preparation of Parethyltoluene and its Derivatives. By GEORGE DEFREN (*Ber.*, 1895, **28**, 2648—2653).—The author has attempted to separate the mixture of ethyltoluenes, obtained by the action of ethylic chloride on toluene in the presence of aluminium chloride, by a method similar to that used for the separation of the xylenes (*Zeit. anal. Chem.*, **32**, 243), but as it did not give good results he prepared parethyltoluene by Fittig's synthetical method, and obtained the following derivatives.

Parethyltoluenesulphonic acid, $\text{C}_6\text{H}_3\text{MeEt} \cdot \text{SO}_3\text{H} + 1\frac{1}{2}\text{H}_2\text{O}$, forms glistening plates, melts at 59 — 60° , and is readily soluble in water. The *barium salt*, $(\text{C}_6\text{H}_3\text{MeEt} \cdot \text{SO}_3)_2\text{Ba} + 2\text{H}_2\text{O}$, crystallises from water in slender needles, and in the anhydrous form is insoluble in ether and in alcohol; the *sodium salt* crystallises with $1\frac{1}{2}\text{H}_2\text{O}$; the *sulphonic chloride* is a yellowish, heavy oil, which solidifies when placed in a freezing mixture, and melts at 3° ; the *sulphonamide* is readily soluble in ether and in alcohol.

Parethyltoluonitrile, obtained by heating dry sodium ethyltoluenesulphonate with potassium cyanide, is a yellowish oil; it begins to boil at 235° , but then rapidly undergoes decomposition, and cannot be hydrolysed by heating with concentrated hydrochloric acid at 200° .

Chloroparethyltoluene, obtained by chlorinating the hydrocarbon in the presence of iodine, is an oily liquid with an agreeable odour, and boils at 200° to 203° ; on further chlorination, it yields the *dichloro*-derivative, which boils at 240 — 243° .

Orthobromoparethyltoluene, obtained by the action of bromine on the

hydrocarbon in presence of iodine, boils at 220—222° (corr.), at the same time undergoing slight decomposition; the *dibromo*-derivative [Me : Et : Br₂ = 1 : 4 : 2 ?] boils at 260—265° (uncorr.).

Chloroparethyltoluenesulphonic acid crystallises in glistening plates, which readily liquefy when exposed to the air. The *barium* salt crystallises with 4H₂O, the *sodium* salt is anhydrous, and the *sulphonic chloride* is a yellow oil which does not become solid at -15°.

Orthobromoparethyltoluenesulphonic acid crystallises in thin plates, yields a *barium* salt, (C₆H₂MeEtBr·SO₃)₂Ba + 5H₂O, a *sodium* salt, C₆H₂MeEtBr·SO₃Na + H₂O, an oily *sulphonic chloride*, and a *sulphonamide* which melts at 143°. J. J. S.

Three Octochlorophenols. By ÉTIENNE BARRAL (*Bull. Soc. Chim.*, 1895, [3], 13, 490—492).—Hexachlorophenol dichloride is the final product of the action of chlorine on phenol in presence of antimonious chloride, and exists in three modifications. The dark brown crystalline product is washed with dilute acid, and recrystallised alternately from light petroleum and chloroform, yielding ultimately a white, crystalline mixture of the three isomerides, melting somewhat indefinitely at 68—70°. The separation is effected by hand, large and sufficiently characteristic crystals of the three varieties being obtained by slow evaporation of the ethereal solution in the cold.

α-Hexachlorophenol dichloride, C₆Cl₈O, obtained in this manner is identical with that prepared by Benedikt and Schmidt by chlorinating pentachlorophenol in acetic acid solution, and it is also prepared by heating hexachlorophenol in sealed vessels at above 210°, or at a somewhat lower temperature in presence of bromine; it crystallises in orthorhombic prisms, and melts at 103·5—104°.

β-Hexachlorophenol dichloride crystallises in flat, orthorhombic prisms, and melts at 89·5—90°. It is converted by fuming sulphuric acid into a *hexachloroquinone*, which has a slight odour of camphor and melts at 87·5—88·5°; this ketone is distinct from that of Zincke and Fuchs, and is converted by phosphorus pentachloride into hexachlorophenol and hexachlorobenzene dichlorides.

γ-Hexachlorophenol dichloride crystallises in monoclinic prisms, as broad as they are long, and melts at 88—89°.

The hexachlorophenol dichlorides are reduced to pentachlorophenol by tin and hydrochloric acid, and are converted into the acetate of that substance by acetic anhydride; they are decomposed at temperatures somewhat above their melting points, into chlorine and products containing perchlorodioxypheylene, but, on the whole, are much more stable than hexachlorophenol, of which they are probably additive derivatives. JN. W.

Formanilide and its Derivatives. By LUDWIG CLAISEN (*Annalen*, 1895, 287, 360—371).—On a former occasion (Abstr., 1895, i, 62), the author traced an analogy between hydroxymethylene compounds, and formanilide, which he represented as hydroxymethyleaniline, NPh:CH·OH, and this view has been accepted by Auwers (Abstr., 1895, ii, 41; compare also 1894, ii, 133) on the ground that in cryo-

scopic behaviour formyl derivatives of primary bases differ from those of secondary bases. The author, however, no longer advocates his former conception of the constitution of formanilide on account of the fact that, unlike the sodium derivatives of hydroxymethylene compounds, sodium formanilide does not yield an alkyl ether when treated with alkylid iodides; moreover, whilst hydroxymethylene compounds boil at a lower temperature than their alkyl ethers, formanilide (b. p. 294°) boils 82° higher than the ethyl ether.

Detailed directions for preparing ethylformanilide (*ethoxymethylenaniline*) from aniline and ethylic orthoformate are to be found in the original paper (compare Comstock and Clapp, *Abstr.*, 1892, 708). In preparing diphenylformamidine (*methenylbis(aniline)*), there is no occasion to heat aniline with ethylic orthoformate in a sealed tube, as stated by Wichelhaus (*Ber.*, 1869, 2, 116), the most convenient method being that adopted in preparing the foregoing substance, using the calculated quantities of material.

When phenylhydrazine, dissolved in glacial acetic acid, is brought into contact with ethylic orthoformate at 0° , formylphenylhydrazide and formazylhydride (*Abstr.*, 1893, i, 83) are produced, the yield of the latter substance being larger than when ethylic formate is employed.

Sodium formanilide is conveniently prepared by heating in a reflux apparatus an ethereal solution of aniline containing sodium, and slowly adding the calculated amount of ethylic formate. Formylphenylhydrazide is obtained by heating sodium (23 grams), dissolved in alcohol (500 grams) with phenylhydrazine (108 grams) and ethylic formate (75 grams) for half an hour on the water bath; one-third of the alcohol is distilled off, and the clear liquid obtained on pouring the residue on to melting ice is acidified with dilute acetic acid, when formylphenylhydrazide (108 grams) separates. M. O. F.

Diazoperhaloids. By ARTHUR R. HANTZSCH (*Ber.*, 1895, 28, 2754—2763).—Nine of the 10 theoretically possible diazoperhaloids RN_2X_3 can readily be obtained (R = an aromatic radicle; X = a haloid atom); attempts to prepare the trichloride have hitherto failed. These compounds are probably constituted according to the diazonium type $N::NRX_3$; they closely resemble the alkali trihaloids, such as KI_3 , $CsBr_3$, H_4NI_3 , &c., of which, in the case of the caesium derivatives, eight of the 10 possible are known, the trichloride and the chlorodiiodide not having been described. The resemblance extends to the colours: the diazotriiodides are bluish-black, have a metallic lustre, and are almost opaque; the diiodobromides are dark reddish-brown, the dibromiodides cherry-coloured, the tribromides orange, and the chlorobromiodides dark yellow; the remaining compounds are less intensely coloured, the dichlorobromides being pale yellow. The colour is also influenced by the presence of substituting groups in the benzene nucleus. The compounds are unstable, but less explosive than the diazonium monohaloids; they are sparingly soluble in water, and generally a portion is decomposed; this property being most marked in the case of the two diiodides, the dibrom- and dichlor-iodides and the chlorobromiodide are much more

stable. Alcohol dissolves them more readily, and less decomposition takes place; in ether, they scarcely dissolve, and undergo slow decomposition.

Diazoparachlorobenzene cyanide, by the action of bromine, is converted, not into the additive compound $C_6H_4Cl \cdot NBr \cdot NBr \cdot CN$, but into the tribromide, which is also formed from parachlorobenzene-diazonium chloride; this does not readily accord with the usual diazo-formula. All attempts, by varying the experimental conditions, to prepare structural isomerides, such as $PhNBr \cdot NCII$ and $PhNCI \cdot NIBr$, or $\begin{array}{c} Ph \cdot N \cdot Br \\ | \\ I \cdot N \cdot Cl \end{array}$ and $\begin{array}{c} Ph \cdot N \cdot Cl \\ | \\ Br \cdot N \cdot I \end{array}$ respectively, have been un-

successful, it is possible that the diazonium radicle $N \equiv NPh$ — is linked to the trihaloid group as a whole rather than to any single atom; this would be similar to the hydrogen-nitrogen linking in the imide group of pyrazole, tetrazole, and probably azoimide. Attempts to eliminate selected haloid atoms from the above compounds, particularly in the absence of solvents which could cause dissociation, were unsuccessful. No pentahaloids corresponding with CsX_5 could be isolated, but evidence of their probable existence is afforded by the fact that all the trihaloids combine with bromine, iodine, bromine iodide, and chlorine iodide and triiodide to form dark coloured unstable oils. The haloids may be employed in considerable excess without the benzene nucleus being attacked; this is in marked contrast with aniline and its derivatives; dimethylaniline rapidly attacks bromine water; trimethylphenylammonium salts, like the diazonium salts, are without action; this also favours the diazonium constitution. Most of the diaziodides are unstable, and are possibly syn-derivatives. *Diazomesitylene iodide*, which will be described later, is exceptional in this respect, and, with alcoholic solution of iodine, yields *mesityldiazonium triiodide*, $C_6H_2Me_3N_2I_3$, which crystallises in dark brown needles with a blue reflex, and decomposes at about 70° .

Benzenediazonium chlorodiiodide, PhN_2ClI_2 , prepared from the diazonium chloride and alcoholic iodine solution in molecular proportion, crystallises in dark violet, lustrous needles, melts at 67° , is stable in dry air, but is quantitatively decomposed by water. The *dichloriodide*, PhN_2Cl_2I , is formed by the action of alcohol on the preceding compound and subsequent precipitation with ether; the action takes place in two stages, a portion of the diiodide is resolved into iodo-benzene, nitrogen, and iodine chloride, this then combines with the remaining diiodide forming iodine and the dichloriodide; the latter is also formed from benzenediazonium chloride and chloriodide, it is stable, crystallises from alcohol in yellow plates, and melts at $86-87^\circ$. The *bromodiiodide*, PhN_2BrI_2 , is prepared like the preceding compounds, and crystallises in lustrous, brownish-red needles. The *dibromiodide*, PhN_2Br_2I , is obtained in a similar manner to the dichloro-derivative, and also from benzenediazonium tribromide and iodine; it forms brown crystals, and decomposes at 77° . The *chloro-dibromide*, PhN_2ClIBr_2 , prepared by the action of benzenediazonium chloride and bromine in chloroform solution, is a reddish-yellow, crystalline powder; it melts at 61° , and is comparatively unstable. The *bromodichloride*, PhN_2BrCl_2 , is formed by the action of chlorine

on the tribromide in chloroform solution; it crystallises from alcohol in pale yellow needles, melts at 63° , and is immediately decomposed by water. The *chlorobromiodide*, PhN_2ClBrI , is formed from the diazonium chloride or bromide by the action of bromine iodide and chlorine iodide respectively; it is deposited in golden needles melting at $80-81^{\circ}$.

Parabromobenzenediazonium bromodiiodide, $\text{C}_6\text{H}_4\text{Br}\cdot\text{N}_2\text{BrI}_2$, can only be prepared at about -15° , and forms brownish-red plates melting at about 79° . The *dibromiodide*, $\text{C}_6\text{H}_4\text{Br}\cdot\text{N}_2\text{Br}_2\text{I}$, is obtained, together with parabromiodobenzene, by heating the preceding compound with alcohol or glacial acetic acid, and also from the diazonium bromide and bromine iodide or iodine; it crystallises in brownish-yellow needles, melts and decomposes at $106-107^{\circ}$. The *chlorobromiodide*, $\text{C}_6\text{H}_4\text{Br}\cdot\text{N}_2\text{ClBrI}$, is comparatively stable, and crystallises in golden needles melting at $111-112^{\circ}$.

The paranitrobenzenediazonium trihaloids are much less stable than the above compounds; attempts to prepare the chlorodiiodide were unsuccessful, as even at very low temperatures nitrogen is evolved and paranitroiodobenzene is formed. *Paranitrobenzenediazonium dichloriodide*, $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\text{Cl}_2\text{I}$, melts and decomposes at 106° . The *chlorobromiodide*, $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\text{ClBrI}$, forms yellow crystals, melts at 93° , and, with alcohol, yields bromoparanitrobenzene. J. B. T.

β -Lactylphenylhydrazide: Phenylhydrazine Citrate and Tartrate. By HENRY J. F. DE VRIES (*Ber.*, 1895, **28**, 2611—2612).— *β -Lactylphenylhydrazide*, $\text{NHPh}\cdot\text{NH}\cdot\text{CO}\cdot\text{CHMe}\cdot\text{OH}$, is formed when phenylhydrazine and lactic acid are heated together at $130-140^{\circ}$; it forms white crystals, which melt at 114.5° . *Phenylhydrazine citrate* melts at 102° . *Phenylhydrazine d-tartrate* probably has the formula, $(\text{N}_2\text{H}_5\text{Ph})_2\text{C}_4\text{H}_6\text{O}_6 + 3\text{H}_2\text{O}$, and turns brown in the air. A. H.

Phenylazocarboxylamide and Phenylazocarboxylic acid. By JOHANNES THIELE (*Ber.*, 1895, **28**, 2599—2601).—Phenylazocarboxylamide, $\text{NPh}\cdot\text{N}\cdot\text{CONH}_2$ (Widman, *Abstr.*, 1895, i, 603), when it is formed in presence of water, crystallises with $2\text{H}_2\text{O}$ as an orange-yellow powder that melts at 84° ; it readily loses its water by deliquescence, or when recrystallised from organic solvents, and then forms red needles melting at 114° . Its (mono-) *potassium derivative* forms dark red plates. *Potassium phenylazocarboxylate*, $\text{NPh}\cdot\text{N}\cdot\text{COOK}$, is obtained by the action of potash on phenylazocarboxylamide, or by the oxidation of phenylsemicarbazide in alkaline solution; it crystallises in orange-red needles, and is decomposed by water.

β -Naphthylazocarboxylamide is obtained, though much less easily than the phenyl compound, by the oxidation of *β -naphthylsemicarbazide*; it forms orange-red crystals, and melts at $137-138^{\circ}$.

C. F. B.

Ketones from Propenyl Compounds. By OTTO WALLACH and F. J. POND (*Ber.*, 1895, **28**, 2714—2722).—If anethoil is converted into the dibromide, and the latter treated with sodium methoxide, an oil is formed which contains the compound, $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{C}(\text{OMe})\cdot\text{CHMe}$;

if the crude product of the action is distilled with steam, *ethyl anisyl ketone*, $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{CH}_2\text{Me}$, is obtained; this melts at $26\text{--}27^\circ$, and boils at $136\text{--}139^\circ$ under 12 mm. pressure, at $265\text{--}270^\circ$ under atmospheric pressure; the *oxime* melts at 74° , the *semicarbazone* at $172\text{--}173^\circ$. When oxidised with permanganate, the ketone yields anisic acid and a ketonic acid, $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{COOH}$, which melts at 75° , and is very soluble in water. When it is heated with strong sulphuric acid at 200° , some propionic acid is formed.

Isosafrole, $\text{CH}_2\text{:O}_2\cdot\text{C}_6\text{H}_3\cdot\text{CH}\cdot\text{CHMe}$, and ethylisoeugenol,



behave in exactly the same way, the ketone formed always containing the carbonyl group directly attached to the benzene ring. The *ketone*, $\text{CH}_2\text{:O}_2\cdot\text{C}_6\text{H}_3\cdot\text{CO}\cdot\text{CH}_2\text{Me}$, melts at 39° , and boils at $153\text{--}154^\circ$ under 13 mm. pressure; the *oxime* melts at 104° . It is probably identical with the ketone obtained by Angeli (Abstr., 1892, 1198), and perhaps also with another obtained by Tonnie's (Abstr., 1888, 264) from anethoil nitrite.

The *ketone*, $\text{OMe}\cdot\text{C}_6\text{H}_3(\text{OEt})\cdot\text{CO}\cdot\text{CH}_2\text{Me}$, melts at 62° , and boils at 155° under 13 mm. pressure; the *oxime* melts at 114° , the *semicarbazone* at 175° . When oxidised, it yields two acids, one sparingly soluble in water and melting at 190° , the other (? ketonic) easily soluble, and melting at $64\text{--}65^\circ$. The ketone is doubtless identical with that obtained by Hell and Portmann (Abstr., 1895, i, 657).

C. F. B.

Etherification and Hydrolysis. By RUDOLF WEGSCHEIDER (*Ber.*, 1895, 28, 2535—2536; compare Abstr., 1895, i, 499).—The author, in reply to Meyer (*Ber.*, 1895, 28, 1798), maintains his former criticism of Meyer's theory of the etherification of substituted ethereal carbonylates. He also criticises Brühl's treatment (*Ber.*, 1895, 28, 1913) of the same question.

A. H.

Dinitrobenzoic acids. By FR. GRELL (*Ber.*, 1895, 28, 2564—2565).—2:5-Dinitrobenzoic acid can be obtained by oxidising with nitric acid at $140\text{--}150^\circ$ the 2:5-dinitrotoluene obtained by Sandmeyer's reaction from 5-nitro-orthotoluidine. In the same way, 2:3-dinitrobenzoic acid can be obtained from 2:3-dinitrotoluene, the latter being obtained when 2-acetotoluidide is nitrated, and the resulting 3-nitro-derivative treated with nitrous acid and cuprous oxide; the acid melts at 201° , the barium salt crystallises with $4\text{H}_2\text{O}$.

C. F. B.

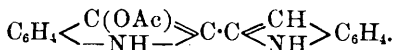
Isocoumarincarboxylic acid. By EUGEN BAMBERGER (*Annalen*, 1895, 288, 134—138; compare Abstr., 1893, i, 592).—In order to establish the identity of the acid obtained by oxidising dihydronaphthol with potassium permanganate (*loc. cit.*), isocoumarincarboxylic acid was reduced with sodium amalgam, the product being identical with dihydroisocoumarincarboxylic acid, as already described.

When isocoumarincarboxylic acid is treated during one hour with boiling, aqueous caustic soda, orthotoluic acid is produced, oxalic acid being formed at the same time. Other ketonic acids undergo analogous decomposition; thus pyruvic acid and phthalonic acid,

$\text{COOH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{COOH}$, yield oxalic acid when treated with boiling, aqueous soda, but benzoylformic acid does not behave in this way.

M. O. F.

The Red Isomeride of Indigotin; Derivatives of Isatin. By EDWARD SCHUNCK and LEO MARCHLEWSKI (*Ber.*, 1895, **28**, 2525—2531; compare *Abstr.*, 1895, i, 288).—The three substances which have been described as red isomerides of indigotin have been proved by the authors to be identical; this identity is further shown by the fact that they all yield the same substance when treated with zinc dust in presence of acetic anhydride and dehydrated sodium acetate. This product crystallises in faintly pink, lustrous needles melting at 204° . It appears to be *acetylundilencin*,



Dimethylindirubin, $\text{C}_6\text{H}_3\text{Me}\langle\text{C}\begin{smallmatrix}\text{CO}\\-\text{NH}-\end{smallmatrix}\rangle\text{C}\cdot\text{C}\langle\text{C}\begin{smallmatrix}-\text{CO}-\\-\text{C}_6\text{H}_3\text{Me}\end{smallmatrix}\rangle\text{NH}$, is formed by the reduction of paramethylisatin chloride. It crystallises in chocolate-brown needles, and closely resembles indirubin.

Isatinmethylphenylhydrazone, $\text{NMePh}\cdot\text{N}:\text{C}\langle\text{C}\begin{smallmatrix}(\text{OH})\\-\text{C}_6\text{H}_4-\end{smallmatrix}\rangle\text{N}$, crystallises in orange needles melting at $172\text{--}173^\circ$; it is strictly analogous to isatinphenylhydrazone, and it is, therefore, probable that both of these substances are true hydrazones, and not azo-compounds, since the "mobile" hydrogen of the hydrazone is replaced by methyl in the methylhydrazone. *Isatinacetylmethylphenylhydrazone* forms yellow needles melting at 145° . *Isatin- β -naphthylhydrazone* crystallises in dark yellow needles melting at 234° .

Isatin readily reacts with orthophenylenediamine, *isatohydrophenazine*, $\text{C}_{14}\text{H}_9\text{N}_3$, being obtained; it is as yet doubtful whether this substance is a derivative of isatin or of pseudo-isatin. It crystallises in yellow needles which melt at $285\text{--}287^\circ$, and can be sublimed; it is stable towards acids and alkalis, and is insoluble in the latter. The *silver salt* is a reddish-brown powder. The *acetyl derivative* melts at 202° .

Metachlorisatohydrophenazine, $\text{C}_{14}\text{H}_8\text{ClN}_3$, is prepared from meta-chlorisatin and orthophenylenediamine, and crystallises in sparingly soluble, yellow needles. Its *silver salt* is an orange coloured precipitate. The *acetyl compound* melts at 215° . A. H.

Reduction Products of Azo-compounds. By PAUL JACOBSON (*Ber.*, 1895, **28**, 2541—2558; compare *Abstr.*, 1895, i, 26).—The main object of the following research was to experimentally determine whether ortho- and meta-methylazobenzene and metazotoluene undergo the normal reaction when converted into benzidine derivatives; all the three compounds were found to yield derivatives of paradiamidodiphenyl. Many of the substances described have already formed the subjects of patents.

I. With W. LISCHKE.—Orthomethylazobenzene is a red oil which boils at $180\text{--}181^\circ$ (corr.) under 20 mm. pressure. The hydrazo-

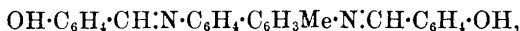
compound melts at 101° . 3-Methylbenzidine [$\text{Me} : (\text{NH}_2)_2 = 3 : 4 : 4'$] is a syrup which could not be obtained crystallised. Its *dibenzylidene derivative*, $\text{CHPh} \cdot \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{N} \cdot \text{CHPh}$, forms yellowish tablets melting at 134° .

4 : 4'-Diiodo-3-methyldiphenyl, $\text{C}_6\text{H}_4\text{I} \cdot \text{C}_6\text{H}_3\text{MeI}$, is obtained by means of the diazo-reaction from methylbenzidine. It forms rosettes of needles, and melts at 109° . When it is distilled with zinc dust, it yields metaphenyltoluene, identical with the hydrocarbon which has been described by Adam (Abstr., 1888, 959). It follows from this, that methylbenzidine has been formed from orthomethylhydrazobenzene in the normal manner.

II. With A. W. NANNINGA.—Metamethylazobenzene is usually prepared (German Patent, No. 54,599) by the elimination of the amido-group from the condensation product formed from diazobenzene chloride and orthotoluidine; it may also be obtained by the condensation of metanitrotoluene with aniline in the presence of alkalis. It crystallises in prisms, melts at 18 – 19° , boils at 175° (pressure = 19 mm.), and has the sp. gr. 1.065 at $20^{\circ}/4^{\circ}$.

Metamethylhydrazobenzene, $\text{NHPh} \cdot \text{NHC}_6\text{H}_4\text{Me}$, crystallises in yellowish needles, and melts at 59 – 61° .

The corresponding 2-methylbenzidine (4 : 4'-diamido-2-methyldiphenyl) cannot be obtained in the crystalline form. The *hydrochloride* forms long needles. The *diacetyl* derivative crystallises in pointed prisms which do not melt when heated to 300° . The *dibenzylidene* derivative crystallises in groups of small needles and melts at 111 – 112° . The *diorthohydroxybenzylidene* derivative,



crystallises in slender prisms which melt indefinitely at about 160° . 4 : 4'-Diiodo-2-methyldiphenyl forms arborescent crystals melting at 114 – 116° . 4 : 4'-Dihydroxy-2-methyldiphenyl crystallises in lustrous plates melting at 155 – 157° . When the diiodo-derivative is distilled with zinc dust, it yields orthophenyltoluene, identical with the hydrocarbon described by Oddo and Curatolo (Abstr., 1895, i, 606). The formation of the benzidine compound in this case is, therefore, normal.

III. With O. FABIAN.—Metazotoluene, together with some of its derivatives, has already been described by Buchka and Schachtebeck (Abstr., 1889, 701). The *dibenzylidene* derivative of the corresponding tolidine, $\text{C}_{12}\text{H}_6\text{Me}_2(\text{N} \cdot \text{CHPh})_2$ [$= 2 : 2' : 4 : 4'$], crystallises in stellate groups of light yellow tablets melting at 172 – 173° . The *diorthohydroxybenzylidene* derivative melts at 198 – 199° . This tolidine was then converted into the diiodo-derivative, and this, without complete purification, distilled with zinc dust. The hydrocarbon produced is converted by oxidation into diphenic acid, and is therefore orthoditolyl. The conversion of the hydrazo-compound into tolidine has, therefore, also proceeded normally in this case.

IV. With K. MICHAELIS, and A. W. NANNINGA.—2 : 4-Dimethylazobenzene, $\text{C}_6\text{H}_3\text{Me}_2 \cdot \text{N}_2\text{Ph}$, prepared from metaxylidine and nitrobenzene, boils at 205 – 215° (pressure = 50 mm.), and has the sp. gr. 1.071 at

20°/4°. The *hydrazo-compound* crystallises in white needles melting at 77—79°.

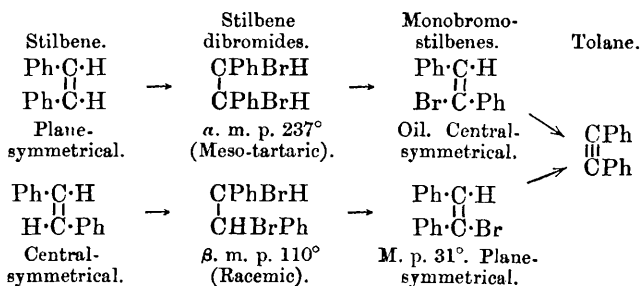
4: 3'-Dimethylazobenzene, $C_6H_4Me \cdot N_2 \cdot C_6H_4Me$, which has been previously obtained by Zincke and Lawson (Abstr., 1886, 795), may also be prepared from paratoluidine and metanitrotoluene. It crystallises in red needles melting at 55°. The corresponding *hydrazo-compound* crystallises in colourless six-sided tablets and melts at 74°.

A. H.

Isomeride of Hydroxydiphenylethylamine. By HENRY G. SÖDERBAUM (*Ber.*, 1895, **28**, 2522—2524).—The author has obtained, in the preparation of hydroxydiphenylethylamine, an isomeric substance which appears to be identical with the compound obtained by Erlenmeyer by the condensation of benzaldehyde with glycocine (Abstr., 1895, i, 596), and by Polonowska by the reduction of benzile-monoxime (Abstr., 1888, 485). It melts at 129°, and forms a *hydrochloride* which at first separates as an amorphous mass, but changes into slender needles. The *platinochloride*, $2C_{14}H_{15}NO, H_2PtCl_6$, is anhydrous, and melts at 213°.

A. H.

Stilbene Dibromides and Monobromostilbenes. By JOHANNES WISLIGENUS and FELIX SEELER (*Ber.*, 1895, **28**, 2693—2703).—When stilbene is treated with bromine in carbon bisulphide solution, two, doubtless geometrically isomeric, dibromides are formed; the less soluble α -compound melts at 237°, the more soluble β -(*iso*)compound at 110—110.5°. The α -compound is always the main product, and so would appear to be the normal additive product of ordinary stilbene, but if that be so, it is remarkable that increase of temperature or of light intensity during the operation causes a larger amount of it to be formed; as a rule the amount of the abnormal product is increased thereby. Either of the two dibromides undergoes a partial conversion into the other when heated. Both yield monobromostilbenes, when treated with alcoholic potash; the α -compound yields an oil, the β -compound crystals melting at 31°. These bromostilbenes both yield toluene when treated with alcoholic potash, but the crystallised compound does this very much more readily than the other, and hence has the hydrogen and bromine atoms in corresponding positions. From this the stereochemical formulæ of the other compounds mentioned can be deduced.



The dibromides are thus represented as derived from isomeric stilbenes; the authors were, however, unable to obtain satisfactory evidence that stilbene does exist in two configurations.

C. F. B.

Formation of Triphenylcarbinol. By HG. FREY (*Ber.*, 1895, 28, 2514—2521).—Sodium decomposes ethylic oxalate into ethylic carbonate and carbonic oxide. When a solution of ethylic oxalate and bromobenzene in ether is treated with sodium, a mixture of hydrogen and carbonic oxide is evolved and triphenylcarbinol is formed together with benzoic acid. It is probable that the bromobenzene is first converted into benzaldehyde or benzophenone by the carbonic oxide and hydrogen in presence of sodium, and that the triphenylcarbinol is obtained from this. The product actually contains a small amount of benzaldehyde, and both this substance and benzophenone yield triphenylcarbinol when they are mixed with bromobenzene in ethereal solution and treated with sodium. The yield obtained from benzophenone is almost quantitative.

The author has attempted to prepare the corresponding derivative from acetone and methylic iodide, but without success, isopropyl alcohol being the chief product. Parabromaniline, moreover, does not yield pararosaniline when treated with sodium and ethylic oxalate, although nitrogen compounds of high melting point are formed.

A. H.

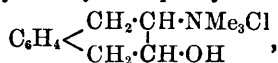
Alicyclic Derivatives of Naphthalene. By EUGEN BAMBERGER, and WILHELM LODTER, [with BERNHARD DEICKE] (*Annalen*, 1895, 288, 74—133; compare *Abstr.*, 1893, i, 591, and 1894, i, 419).—The paper contains a detailed account of the preparation and properties of those derivatives which have been already described (*loc. cit.*), and the following facts (obtained in conjunction with B. Deicke) are also recorded.

The *hydrochloride* and *picrate* of 2-dimethylamido-3-hydroxy-tetrahydronaphthalene, $C_6H_4 < \begin{smallmatrix} CH_2 \cdot CH \cdot NMe_2 \\ | \\ CH_2 \cdot CH \cdot OH \end{smallmatrix}$, melt at 180—181° and 182° respectively; the *aurochloride* crystallises in lustrous, yellow needles, and the *platinochloride* forms orange-red leaflets. The *methiodide* crystallises from water in long, lustrous prisms, and melts at 201°, and the *benzoate* crystallises in aggregates of needles; the latter has powerful toxic properties.

The *hydrochloride* and *picrate* of 2-diethylamido-3-hydroxytetrahydronaphthalene (diethyltetrahydronaphthylalkine) melt at 167—170° and 170·5—171° respectively; the *aurochloride* crystallises in yellow leaflets or needles, and the *platinochloride* is orange-red. The *methiodide* crystallises in white leaflets and melts at 151·5°, and the *benzoate* separates from alcohol in reddish-yellow, lustrous needles; the latter forms a *picrate* which crystallises in yellow needles.

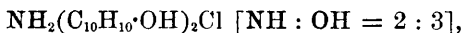
The *aurochloride* of 2-piperidyl-3-hydroxytetrahydronaphthalene crystallises in yellow leaflets, and the *platinochloride* separates from water in orange-red crystals.

Trimethyl-3-hydroxytetrahydronaphthylammonium chloride,



forms crystals belonging to the monoclinic system: $a:b:c = 1.0854:1:0.5081$; $\beta = 67^\circ 43'$. Precipitates similar to those formed by choline are produced when the chloride is treated with common reagents for the detection of alkaloids. The *platinochloride* crystallises in orange needles and melts at $222\text{--}223.5^\circ$; the *aurochloride* separates from water in lustrous, golden-yellow leaflets, and melts at $152\text{--}154^\circ$. The *picrate* crystallises in flat needles, and melts at $161\text{--}162^\circ$.

The *hydrochloride* of bishydroxytetrahydronaphthylamine,



separates from alcohol on adding ether in lustrous, white needles. The *platinochloride*, which is only sparingly soluble in cold water, crystallises in light-orange needles which melt and decompose at 235° ; the *aurichloride* crystallises in lustrous, yellow leaflets.

The *platinochloride* of 2 : 3-hydroxytetrahydronaphthylamine crystallises in reddish-yellow prisms, and the *aurichloride* forms needles. The *picrate* dissolves in hot water, and crystallises in needles.

M. O. F.

Tetralkyldiamidoazonaphthalenes. By PAUL COHN (*Monatsh.*, 1895, 16, 798—806).—*Tetramethyldiamido- α -azonaphthalene* is obtained on passing nitric oxide for two or three weeks through an alcoholic solution of α -dimethylnaphthylamine (compare Lippmann and Fleissner, *Abstr.*, 1883, 55, 184, 868, 1100). It separates from alcohol, in which it is only sparingly soluble, in brownish-red, dichroic crystals, sinters at 140° , and melts at 145° ; it yields a yellowish-brown crystalline *picrate*, $\text{C}_{24}\text{H}_{24}\text{N}_4 \cdot 2\text{C}_6\text{H}_2(\text{NO}_2)_3\text{OH}$, which is almost insoluble in boiling organic solvents, and, on reduction with stannous chloride in hydrochloric acid solution, forms paradimethylnaphthylamine (compare Friedländer and Welmans, *Abstr.*, 1889, 150).

Tetrethyldiamido- α -azonaphthalene, obtained in a similar manner to that employed in preparing the tetramethyl compound, crystallises in reddish-yellow, rhombic plates, gives, with hydrochloric acid, a blue coloration, which is destroyed on the addition of water, and melts at 143° to a reddish-brown liquid; it yields a *picrate*,



which crystallises in reddish-brown needles, is sparingly dissolved by ordinary solvents, and melts and decomposes at 200° .

Dipropyl- α -naphthylamine, $\text{C}_{16}\text{H}_{21}\text{N}$, obtained on heating a mixture of α -naphthylamine, potash solution, and normal propylic iodide under pressure at 180° , boils at 300° , has a specific gravity of 0.9935 at 20° , yields a *hydrochloride*, $\text{C}_{16}\text{H}_{21}\text{N} \cdot \text{HCl} \cdot \text{H}_2\text{O}$, which crystallises in white needles, a *hydriodide*, $\text{C}_{16}\text{H}_{21}\text{N} \cdot \text{HI}$, which crystallises in yellow, felted needles, and a yellow *platinochloride*, $(\text{C}_{16}\text{H}_{21}\text{N})_2 \cdot \text{H}_2\text{PtCl}_6$, which darkens at 160° , and melts and decomposes at 212° . No definite azo-compound could be obtained by the action of nitric oxide on dipropyl- α -naphthylamine.

G. T. M.

Terpenes and Ethereal Oils. Phellandrene. By OTTO WALLACH and AD. HERBIG (*Annalen*, 1895, **287**, 371—384; compare Abstr., 1887, 965; 1888, 1204).—The result of the author's investigation shows that reduction of phellandrene nitrite gives rise to optically active tetrahydrocarvone, tetrahydrocarveole, and tetrahydrocarvylamine, the inactive modifications of which have been already described (Abstr., 1894, i, 44) as arising from carvenone (Abstr., 1895, i, 622), on reducing it with sodium and alcohol; on preparing racemic mixtures of the compounds from *d*- and *l*-phellandrene, inactive tetrahydro-derivatives of the carvone series are obtained.

Phellandrene nitrite, which melts at 105°, is prepared in the following manner; 100 grams of hydrocarbon, rich in phellandrene, are placed in a beaker surrounded by a freezing mixture, along with 400 grams of petroleum, and covered with dilute sulphuric acid, prepared by mixing 37 grams of the concentrated acid with twice its volume of water; 230 grams of a 44 per cent. solution of sodium nitrite is then slowly added, the temperature being maintained below 4°, and the liquid gently stirred from time to time. Eucalyptus oil was employed as the source of *l*-phellandrene, bitter fennel oil being used when derivatives of *d*-phellandrene were required.

When phellandrene nitrite is treated with alcoholic sodium ethoxide, it becomes red, heat being generated and nitrous oxide liberated; in this way, a pale yellow oil is obtained, which boils at 134—138°, and has a penetrating odour; it is identical with the "nitrophellandrene" described by Pesci (Abstr., 1886, 1038). On reducing phellandrene nitrite, or the foregoing compound dissolved in absolute alcohol, with sodium, the ketone, $C_{10}H_{16}O$, the alcohol $C_{10}H_{20}O$, and the base $C_{10}H_{16}NH_2$, are obtained. The ketone boils at 90—100° under a pressure of 15 mm., and yields a dextrorotatory *oxime*, which crystallises in needles, and melts at 97—98°; the *semicarbazone* melts at 185—187°. The alcohol (tetrahydrocarveole) is obtained on reducing the ketone with sodium and alcohol; it boils at 100—104° under a pressure of 12 mm. The base (*tetrahydrocarvylamine*, Abstr., 1894, i, 44) boils at 210—212°, and absorbs carbonic anhydride. The *hydrochloride* melts at 199—204°, and the *acetyl* derivative at 158—159°; the *carbamide* and *phenylcarbamide* melt at 201—203° and 185—186° respectively. When sodium nitrite is added to a feebly acid solution of the hydrochloride, the alcohol is produced, and this substance, on oxidation, yields the ketone.

The authors discuss the constitution of phellandrene. M. O. F.

Pinole. By OTTO WALLACH (*Ber.*, 1895, **28**, 2708—2713).—The author has modified the formula he previously gave to pinole (Abstr., 1895, i, 59), and now regards $CH \begin{array}{c} \text{CH}_2\text{CH:CMc} \\ \text{CH}_2 \\ \text{CMc}_2\text{---O} \end{array} CH$ as the most

probable, although it does not satisfactorily explain all the reactions; in deducing it, regard was had to the fact that terpineole appears to have an hydroxyl group in a side chain.

If pinole glycol is prepared from pinole by direct oxidation, and also by means of the dibromide of the latter, the properties of the two samples are not quite identical.

The ketone, $C_{10}H_{16}O$, prepared by reducing pinole tribromide (*loc. cit.*) in acid solution, has been obtained pure by means of its semicarbazone; it boils at $214-217^\circ$; at 20° its sp. gr. = 0.916, and index of refraction $n_D = 1.46603$; the semicarbazone melts at 158° ; the oxime boils at 150° under 15 mm. pressure, and can be reduced to a base $C_{10}H_{17}NH_2$, the hydrochloride of which can be transformed into a carbamide, $C_{10}H_{17}NH \cdot CO \cdot NH_2$, melting at 186° . The ketone probably contains one ethylene linking, possibly in a side chain in which it is probable that the oxygen atom also is contained. The alcohol, $C_{10}H_{18}O$, obtained by reducing the pure ketone, boils at 108° under 15 mm. pressure, has sp. gr. = 0.913, and index of refraction $n_D = 1.47292$ at 18° . If pinole tribromide is treated with silver acetate in the cold, a compound, $C_{10}H_{17}Br_2O \cdot OAc$ is formed; if heat is employed, an acetate containing no bromine is obtained, the semicarbazone of which melts at $177-178^\circ$. C. F. B.

Oxidation Products of Dihydrocarvone. By OTTO WALLACH (*Ber.*, 1895, 28, 2703—2707).—When dihydrocarvone is oxidised, two ketones are formed, in addition to various acids, including oxalic acid and an acid that melts at $203-204^\circ$, and contains 59.43 and 8.38 per cent. of carbon and hydrogen respectively. The ketone formed in larger quantity melts at $115-120^\circ$, and boils at about 200° under 100 mm. pressure; it is a *ketoglycol*, $C_{10}H_{16}O_3$, the *oxime* of which, $C_{10}H_{16}O_2 \cdot NOH$, melts at 202° , and the *semicarbazone* at 187° ; when boiled for a long time with dilute sulphuric acid, it yields a *ketone*, boiling at 220° , the *semicarbazone* of which melts at 206° . The second of the two original ketones boils at about 130° under 10 mm. pressure, and solidifies in a freezing mixture; it is a *diketone*, $C_9H_{14}O_2$; its *oxime* and *semicarbazone* melt at 195° and $203-204^\circ$ respectively; it can be obtained from the ketoglycol by further oxidation. C. F. B.

Camphoronic acid. By ARNOLD HESS (*Ber.*, 1895, 28, 2687—2693).—Pure camphoronic acid, $C_9H_{14}O_6$, melts at $148-150^\circ$ when it is placed in a bath at 136° , and the latter rapidly heated. When it is slowly heated, starting from the ordinary temperature, it is converted for the most part into the anhydride.

It yields a *triethylic*, together with the diethylic, salt when its solution in absolute alcohol is saturated with gaseous hydrogen chloride; it boils at $295-300^\circ$.

When the diethylic salt is treated with alcoholic ammonia, it yields ammonium ethylic camphoronamate,



melting at $144-145^\circ$; this can also be obtained by the action of ammonia on ethylic anhydrocamphoronate, $O \cdot C_2O_2 \cdot C_6H_{11} \cdot COOEt$. When boiled with aqueous alkalis, it yields *camphoronimic acid*, $NH \cdot C_2O_2 \cdot C_6H_{11} \cdot COOH$, melting at 210° . When the above-mentioned diethylic salt is heated at $120-130^\circ$ with alcoholic ammonia, or when a benzene solution of anhydrocamphoronic acid is saturated with ammonia and then heated at 140° , ammonium camphoronimate, $NH \cdot C_2O_2 \cdot C_6H_{11} \cdot COONH_4$, melting at 175° , is formed; this only loses half of its nitrogen when boiled with aqueous alkalis. By heating

triethylic camphoronate with alcoholic ammonia at 170—190°, a few crystals, melting at 210—218°, were obtained; these were possibly camphoronimic amide, $\text{NH}\cdot\text{C}_2\text{O}_2\cdot\text{C}_6\text{H}_{11}\cdot\text{CONH}_2$.
C. F. B.

Compounds from Lichens. Atranoric acid and Substances accompanying it. By WILHELM ZOFF (*Annalen*, 1895, **288**, 38—74; compare Abstr., 1895, i, 297).—Atranoric acid is the substance first isolated from *Lecanora atra* (Hudson) by Paternò and Ogliastro (this Journal, 1877, ii, 986); its presence in *Cladonia rangiformis* (Schaeerer) and *Stereocaulon vesuvianum* (Pers.) has been since observed by Paternò, and its existence in the dissimilar groups, to which the first-named lichen and the last two belong, has led the author to conduct a systematic search for atranoric acid among 33 different varieties. The investigation has revealed the presence of this acid in the lichens *Stereocaulon alpinum* (Laurer), *S. coralloides* (Fries), *S. incrustatum* (Flörke), *S. denudatum* (Flörke), *var. genuinum* (Fries), *S. tomentosum* (Fries), *S. pileatum* (Acharius), *S. condensatum* (Hoffmann), *S. paschale* (L. and Fries), *S. virgatum* (Ach.), *forma primaria* (Wainio), *S. ramulosum* (Ach.), *Physcia cæsia* (Hoffmann), *P. pulverulenta* (Schreber), *var. β-pityrea* (Ach.), *P. endococcina* (Körber), *P. tenella* (Ach.), *P. alpolia* (Ach.), *Anaptychia ciliaris* (L.), *A. speciosa* (Wulf), *Parmelia encausta* (Sommerfelt), *P. pertusa* (Schrk.), *Parmeliopsis hyperopta* (Ach. and Nyl.), *Hæmatomma coccineum* (Dickson), *Placodium saxicolum* (Poll.), and *P. melanaspis* (Ach. and Fries), in addition to those already mentioned.

The cortex of the thallus is stained yellow by alkalis in the case of those species which contain an appreciable amount of atranoric acid, the coloration being very feeble when the acid is present in small quantity; the test, however, is not trustworthy, as a yellow stain with alkalis may arise from the presence of evernic or thamnolic acids. The lichens *Hæmatomma ventosum* (L.), *Placodium radiosum* (Hoffmann), *Cladonia cornuta* (Ach.), *C. gracilis* (L.) *forma chordalis* (Flörke), *C. g.*, *forma aspera*, *C. macilenta* (Ehrb.), *C. furcata* (Hudson) *forma polyphylla* (Flörke), and *C. squamosa* (Hoffmann), do not contain atranoric acid, and *Placodium crassum* (Hudson), identical with *Psoroma crassum*, *var. caespitosum* (Schaeerer), contains only a trace of it.

Atranoric acid, $\text{C}_{19}\text{H}_{18}\text{O}_8$, has been already described by Paternò and Ogliastro (*loc. cit.*); it separates from chloroform in crystals several millimetres in length, and melts at 195—197°. The crystals belong to the rhombic system; $a : b : c = 0.7773 : 1 : 1.2808$. Atranoric acid yields with alkalis a yellow solution, from which it is precipitated by carbonic anhydride; a yellow coloration is developed on dissolving the substance in concentrated sulphuric acid, and the alcoholic solution becomes purple-red with ferric chloride.

Hæmatommic acid, $\text{C}_{11}\text{H}_{12}\text{O}_5$, is obtained by heating atranoric acid (1 gram) with absolute alcohol (40 c.c.) in a sealed tube at 150° for one hour; it crystallises from dilute alcohol in snow-white, silky needles, and melts at 113—114°. It is exceedingly soluble in hot alcohol, and also dissolves in cold ether, chloroform, and benzene, whilst cold alcohol and light petroleum dissolve it but sparingly; the substance dissolves in alkalis and alkali carbonates, forming a yellow

solution, from which it is precipitated by carbonic anhydride, and the alcoholic solution develops a purple-brown coloration with ferric chloride. When an alcoholic solution of atranoric acid is boiled for many hours in a reflux apparatus, hæmatommic acid is produced; it is, therefore, undesirable to employ boiling alcohol in recrystallising atranoric acid, and prolonged treatment of the lichens with boiling alcohol is to be avoided. Hæmatommic acid has been isolated from the lichens *Hæmatomma coccineum* and *Physcia cæsia*.

Hæmatommenic acid, $C_{21}H_{22}O_{10}$, is obtained by heating atranoric acid (9.5 grams) with methylic alcohol (20 c.c.) in a sealed tube at 150° for one hour; it crystallises from a mixture of methylic alcohol and chloroform in thread-like aggregates of colourless needles, and melts at $146-147^{\circ}$. The solution in alkalis and alkali carbonates is yellowish-green, and the acid is precipitated by carbonic anhydride.

Ommatic acid is formed when atranoric acid is heated with propylic alcohol in a sealed tube at 150° for one hour; it melts at 75° , and dissolves in alkalis and alkali carbonates, forming a yellow solution.

In addition to the lichens already mentioned (Abstr., 1895, i, 298), *Lecanora* (*Zeora*) *sordida*, *Hæmatomma coccineum*, and *Placodium saxicolum* contain zeorin, which crystallises from chloroform or absolute alcohol in hexagonal double pyramids; it melts at $247-252^{\circ}$, and is insoluble in hot alkalis. When treated with boiling alcohol and hydrochloric acid, it yields *zeorinin*, which crystallises in colourless, lustrous leaflets, and melts at $182-184^{\circ}$; this is insoluble in alkalis, and dissolves in concentrated sulphuric acid with development of a yellow coloration.

Usnic acid has been isolated from *Hæmatomma coccineum* and *H. ventosum*, whilst the lichens *Stereocaulon coralloides*, *S. incrustatum*, *S. vesuvianum*, and *S. denudatum* contain psoromic acid.

Placodin is a copper-red substance obtained from *Placodium melanaspis* (Ach. and Fries), identical with *P. inflatum* (Körber); it crystallises from absolute alcohol in thin, pleochroic plates, and melts and decomposes at 245° . It dissolves with difficulty in ether and chloroform, and is nearly insoluble in benzene; the solution in caustic soda is violet-brown, and concentrated nitric acid dissolves it with development of a yellow coloration.

Stereocaulic acid is isolated from *Stereocaulon alpinum* and *Lepora chlorina*, and crystallises from alcohol in white needles melting at $200-201^{\circ}$; it dissolves with difficulty in alcohol, ether, benzene, and chloroform, and carbonic anhydride does not precipitate the acid from its solution in sodium carbonate, which is yellow. The alcoholic solution develops a violet coloration with ferric chloride.

M. O. F.

Nitro-derivatives of Pyridine. By HUGO WEIDEL and ERNST MURMANN (*Monatsh.*, 1895, 16, 749-759).—The authors obtain pyridine- β -sulphonic acid, in the exceptionally high yield of from 45 to 65 per cent., by the sulphonation of pyridine in presence of anhydrous aluminium sulphate with 33 per cent. anhydro-sulphuric acid at $330-350^{\circ}$. The sulphonic acid is first converted into β -hydroxypyridine (m. p. 129°), and subsequently into its acetyl derivative,

and the latter is nitrated by the addition of nitric acid to an ice-cold solution in acetic anhydride; the action is then completed at the ordinary temperature, the acetic anhydride removed by distillation under diminished pressure, and the residue hydrolysed with sodium hydroxide. On adding hydrochloric acid to the product, a precipitate is obtained which, on exhaustion with boiling water, leaves an insoluble *nitro-β-hydroxypyridine*. This crystallises from alcohol in dull, yellow needles, and melts and decomposes at 295—298° (uncorr.). The aqueous solution, on exhaustion with ether, yields a *dinitro-β-hydroxypyridine* which crystallises from the ethereal solution in dull, yellow needles, and melts at 133° (uncorr.). A second *nitro-β-hydroxypyridine* crystallises from the aqueous solution in pale, lemon-yellow plates, and melts at 210—211° (uncorr.).

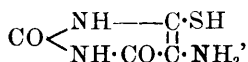
G. T. M.

Direct Introduction of Hydroxyl-groups into Hydroxyquinolines. By JULIUS DIAMANT (*Monatsh.*, 1895, 16, 760—772).—When 1-hydroxyquinoline is heated at 380°, with 10 times its weight of caustic soda and a little water, hydrogen escapes, and 1 : 2'-*dihydroxyquinoline*, $C_9H_7NO_2$, is formed; this crystallises from water in scales, melts with partial decomposition and sublimation at a temperature above 260°, and gives a dirty green coloration with ferric chloride. The *hydrochloride*, $C_9H_7NO_2 \cdot HCl + H_2O$, crystallises in yellowish-white needles or scales, and is very unstable. The *acetyl derivative*, $C_9H_6NO_2Ac$, forms crystalline scales, and melts at 244—247°. On oxidation with potassium permanganate in alkaline solution, the dihydroxyquinoline yields 6-hydroxyquinolinic acid, thus showing that the second hydroxyl-group is in the 2' position.

Trihydroxyquinoline, $C_9H_7NO_3[(OH)_3 = 1 : 2' : ?]$, obtained on further heating the above-described dihydroxyquinoline with excess of caustic soda at 380°, crystallises in long, colourless needles; it is almost insoluble in ordinary solvents, but dissolves in borax solution and in alkalis, has an intensely sweet taste, and gives with ferric chloride a dirty green solution, which is turned brown by sodium carbonate. Trihydroxyquinoline may also be obtained by long-continued heating of hydroxyquinoline with excess of potash.

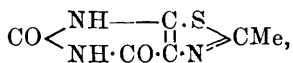
G. T. M.

Formation of Thiazole Derivatives from Uric acid. By HUGO WEIDEL and LADISLAUS NIEMIŁOWICZ (*Monatsh.*, 1895, 16, 721—748).—When uric acid (2.5 grams) and ammonium hydrosulphide (15 c.c. of a solution obtained by adding 1 vol. of commercial ammonia to 2 vols. previously saturated with hydrogen sulphide) are heated together for four hours at 185°, 3-*amidouracyl 2-hydrosulphide*,



is formed. It crystallises from dilute acetic acid and from strong hydrochloric acid in slender needles, which do not melt at 300°, forms an unstable anhydrous *ammonia compound* having the composition $C_4H_5N_3SO_2 \cdot NH_3$, and on the addition of bromine yields uranil, isobarbituric acid, and other substances. On heating with a large excess

of acetic anhydride, amidouracyl hydrosulphide yields the crystalline *acetyl* derivative, $C_6H_7N_3SO_3$, which is soluble in water, amyl alcohol and acetic acid, with partial decomposition, and melts and decomposes at a temperature above 300° . On treatment with water, or better, with a dilute alkaline solution, the acetyl compound yields the *ureide* of μ -methyl- β -oxythiazole- α -carboxylic acid,

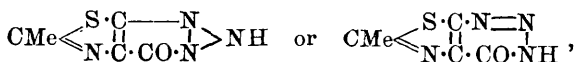


which crystallises in felted masses of small needles, is soluble in water containing acids and alkalis, dissolves sparingly in alcohol and ethylic acetate, and gives the following salts. An *ammonium salt*, $C_6H_7N_3SO_2 \cdot NH_4 \cdot OH$, crystallising in hair-like needles; a *sodium salt*, with $2H_2O$, crystallising in colourless needles; a *barium salt*, and an anhydrous crystalline *silver salt*, $C_6H_6N_3SO_2 \cdot Ag$. When the *ureide* or its acetyl derivative is boiled with acetic anhydride and sodium acetate until no more carbonic anhydride escapes, and the excess of acetic anhydride is distilled off, the residue contains β -acetyl-amido- μ -methylthiazole- α -carboxylonitrile. This is insoluble in cold chloroform, but dissolves in the boiling solvent, from which it crystallises on cooling in long needles, and, when quickly heated, melts at $280-285^\circ$, undergoing partial sublimation. The residue also occasionally contains the β -acetyl-amido- μ -methylthiazole- α -carboxylacetamide, which dissolves in cold chloroform and in water, melts at $176-178^\circ$ (uncorr.), and, on further treatment with acetic acid and sodium acetate, gives the nitrile $C_7H_7N_3SO$. Each of these products from the residue is converted by dilute hydrochloric acid into β -amido- μ -methylthiazole- α -carboxylamide, $C_7H_7N_3SO + 2H_2O$, which crystallises in yellowish-white, monoclinic plates, $[a : b : c = 2.783 : 1 : 1.278]$, is only sparingly soluble in cold water, melts with decomposition at a temperature above 300° , and, on fusion with potassium hydroxide at $260-280^\circ$, yields a crystalline mixture from which two substances were isolated, one soluble in alcohol and the other insoluble. The insoluble substance, formed only in small quantity,

is β -amido- μ -methylthiazole- α -carboxylic acid, $CMe < \begin{array}{c} S \cdot C \cdot NH_2 \\ | \quad | \\ N \cdot C \cdot COOH \end{array} >$. It

crystallises from water, in which it is fairly soluble, in scales, and decomposes at 200° . The soluble portion is apparently the *hydrochloride* of β -amido- μ -methylthiazole, $CMe < \begin{array}{c} S \cdot C \cdot NH_2 \\ | \quad | \\ N \cdot CH \end{array} >$, which is readily dissolved by water, the solution giving an intense cherry-red coloration with ferric chloride, crystallises in scales, and decomposes at 250° .

Azido- μ -methylthiazole- α -carboxylic acid,



which crystallises in yellow scales and decomposes at $270-280^\circ$, is obtained on dissolving β -amidomethylthiazolecarboxylamide in hydrochloric acid, adding the requisite quantity of potassium nitrite,

boiling the solution, evaporating in a vacuum, and finally extracting with alcohol. G. T. M.

Tetrazole Derivatives. By JOHANNES THIELE and HARRY INGLE (*Annalen*, 1895, **287**, 233—265; compare *Abstr.*, 1892, 1295, and 1893, i, 440).—*Amidotetrazole* is the name by which the authors now refer to amidotetrazotic acid (*loc. cit.*), which has the constitution, $\begin{array}{c} \text{N}-\text{N} \\ \parallel \quad \parallel \\ \text{N}\cdot\text{NH} \end{array} > \text{C}\cdot\text{NH}_2$. The *cyanate* is obtained by adding potassium cyanate to an aqueous solution of the hydrochloride; it melts above 250° , and dissolves in dilute hydrochloric acid with liberation of carbonic anhydride, having the odour of cyanic acid. Boiling water decomposes the cyanate, giving rise to carbonic anhydride, ammonia, and amidotetrazole; an alcoholic solution of aniline yields phenyl-carbamide. *Benzoylamidotetrazole* dissolves readily in alkalis, and melts and decomposes above 250° ; the *acetyl* derivative crystallises in white leaflets melting at 269° , and has a strongly acidic reaction. Fuming hydrochloric acid does not attack amidotetrazole at 160 — 170° , but at 200 — 210° carbonic anhydride, ammonia, nitrogen, and hydrazine are formed, the last-named being produced in theoretical quantity.

In preparing benzylidenetetrazylhydrazine (*loc. cit.*), an improved yield is obtained by regulating the quantity of hydrochloric acid in such a manner that at the conclusion of the operation excess of this agent is a minimum.

Triacetyltetrazylhydrazine, $\text{NAC}_2\cdot\text{NAC}\cdot\text{C} \begin{array}{c} \text{N}-\text{N} \\ \parallel \quad \parallel \\ \text{NH}\cdot\text{N} \end{array}$, crystallises from glacial acetic acid, and sinters at 140 — 150° , melting at 192° ; it is strongly acidic, and does not develop a red coloration with ferric chloride. *Acetophenonetetrazylhydrazone* is obtained from aqueous tetrazylhydrazine hydrochloride and alcoholic acetophenone; it melts at 235° , and dissolves readily in alkali carbonates. *Aceton-tetrazylhydrazone* is prepared from tetrazylhydrazine hydrochloride and acetone in presence of sodium acetate; it crystallises from water, and melts at $181\cdot5^\circ$. *Tetrazylsemicarbazide* is formed on mixing warm, aqueous solutions of potassium cyanate and tetrazylhydrazine hydrochloride; it melts at 211° if slowly heated, at 218° when the temperature rises rapidly. The semicarbazide is acidic and strongly reducing, and is sparingly soluble in cold water; an alkaline solution of potassium permanganate oxidises it to tetrazolazocarboxylic acid, of which the *sodium* derivative was precipitated, ammonia being liberated at the same time.

Tetrazylazoimide (*diazotetrazoleimide*), $\begin{array}{c} \text{N}-\text{N} \\ \parallel \quad \parallel \\ \text{N}\cdot\text{NH} \end{array} > \text{C}\cdot\text{N} < \begin{array}{c} \text{N} \\ \parallel \\ \text{N} \end{array}$, is obtained by adding 5 c.c. of concentrated hydrochloric acid mixed with ice to an ice-cold solution of tetrazylhydrazine (2·3 grams) and sodium nitrite (2 grams); it crystallises from benzene in beautiful white needles. When rubbed slightly, or on heating gently, it explodes with greater violence than silver azoimide; it dissolves readily in water and acetone, but is insoluble in petroleum or ether,

and yields azoimide when treated for several hours with boiling concentrated potash. The *silver* derivative is insoluble in cold, dilute, nitric acid, and explodes violently in the moist state; the *ammonium* derivative is a white powder, obtained on passing dry ammonia into a solution of tetrazylazoimide in benzene, and does not explode with greater violence than gunpowder. The ammonium salt is very soluble in water and methylic alcohol, but dissolves less readily in benzene. Fuming nitric acid decomposes tetrazylhydrazine at 170° , giving rise to hydrazine, carbonic anhydride, and nitrogen.

Dihydrobenzylidenetetrazylhydrazine is obtained by reducing benzylidenetetrazylhydrazine with sodium amalgam; it crystallises from alcohol, and melts and decomposes at $187-191^{\circ}$. The *sodium* derivative is colourless, and crystallises from dilute alcohol. The dihydro-derivative differs from benzylidenetetrazylhydrazine in dissolving in dilute mineral acids, and forming a *sulphate* which is sparingly soluble in cold water; it is, moreover, readily oxidised by mercuric oxide or an ammoniacal silver solution, whilst these agents attack benzylidene-tetrazylhydrazine slowly when heated. When the dihydro-compound is treated with boiling hydrochloric or sulphuric acid, a small quantity of benzaldehyde is formed, but at 160° hydrochloric acid gives rise to benzylidene chloride and hydrazine. Acetonetetrazylhydrazone is indifferent towards sodium amalgam.

When sodium diazotetrazolate (*loc. cit.*) is reduced with alcohol, tetrazole is produced; this crystallises from ethylic acetate in aggregates of needles or leaflets, and melts at 156° (compare Bladin, *Abstr.*, 1892, 1009). On heating tetrazole with hydrochloric acid for three hours at 200° , ammonium chloride is formed, but no hydrazine; it is completely decomposed by hot, concentrated sulphuric acid, yielding nitrogen and carbonic oxide. The *sodium* derivative of tetrazole contains $1\text{H}_2\text{O}$, and crystallises in thin prisms, which dissolve very readily in water. The *barium* derivative contains $3\frac{1}{2}\text{H}_2\text{O}$, and crystallises in large, transparent prisms, which become nearly anhydrous in the exsiccator; it belongs to the rhombic system, and has $a:b:c = 0.5689:1:0.7217$. The conductivity constants of tetrazole, of the sodium derivative, and of amidotetrazole have been determined.

Methylamidomethyltetrazole, $\text{NHMe}\cdot\text{C}\begin{smallmatrix} \text{N} \\ \diagup \\ \text{NMe} \end{smallmatrix} \begin{smallmatrix} \text{N} \\ \diagdown \\ \text{N} \end{smallmatrix}$, is obtained by heat-

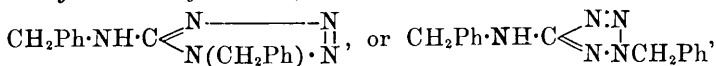
ing anhydrous amidotetrazole (10 grams) with methylic iodide for three hours at $160-165^{\circ}$; it crystallises from ethylic acetate in leaflets, and begins to decompose at 80° . The substance is very hygroscopic, and its solution is strongly alkaline. The *hydrochloride* crystallises from alcohol in white needles, and melts and decomposes at 241° ; the *picrate* melts and decomposes at 203° . The *aurochloride* crystallises from water in large plates, and melts at 164° ; the *platinochloride* crystallises from alcohol in golden-yellow needles, and from water in large prisms, melting at 200° . The *nitrosamine* forms yellow needles, and yields nitrous acid under the influence of dilute mineral acids, nitrogen being evolved on treating it with potash.

Methylamidotetrazole crystallises from water in white needles, and melts at $218-220^{\circ}$; the aqueous solution is neutral. *Ethylamido-*

ethyltetrazole hydrochloride is very soluble in water and alcohol, and forms white needles melting at 232—233°.

α -*Benzylamidotetrazole* is obtained by boiling benzylic chloride (2 mols.) with amidotetrazole (2 mols.), sodium carbonate (1 mol.), water, and alcohol, until the odour of benzylic chloride is no longer perceptible; it melts at 191—192°, and is neutral. β -*Benzylamidotetrazole*, $\text{CH}_2\text{Ph}\cdot\text{NH}\cdot\text{C}\begin{smallmatrix} \text{N} & \text{N} \\ \parallel & \parallel \\ \text{NH} & \text{N} \end{smallmatrix}$, is formed on heating amidotetrazole (10 grams) with benzylic chloride (40 grams), caustic potash (50 grams), and dilute alcohol, for six hours; it melts at 181°, and dissolves in alkalis.

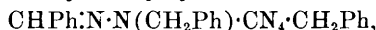
Benzylamidobenzyltetrazole,



arises from the action of boiling benzylic chloride on anhydrous amidotetrazole, and is also obtained as a bye-product in the preparation of α -benzylamidotetrazole; it separates from alcohol and ether in lustrous crystals, and melts at 88.5°. The substance has an alkaline reaction. The *hydrochloride* crystallises in needles, and melts at 208—209°, and the *nitrate* at 122°; the latter salt and the *sulphate*, which melts at 173°, are sparingly soluble, and the *nitrite* crystallises from ether and melts at 108°. The *nitrosamine* crystallises in yellow needles melting at 105°, and when treated with boiling water yields *benzylloxybenzyltetrazole*, which crystallises from alcohol in small needles, and melts at 106°.

β -*Amidodibenzyltetrazole* is most conveniently prepared by heating amidotetrazole (5 grams), with caustic potash (15 grams), benzylic chloride (30 grams), and dilute alcohol in a reflux apparatus for two hours, adding a further quantity of caustic potash (10 grams), and again heating for two hours, or until the odour of benzylic chloride is no longer perceptible; it is also formed in the preparation of α - and β -benzylamidotetrazole. It crystallises from alcohol in lustrous needles, and melts at 169—170°; it is a neutral substance, and when oxidised in acid solution with potassium permanganate yields benzaldehyde. The *nitrosamine* crystallises from alcohol in lustrous, yellow plates, and melts at 97—98°.

Benzylbenzylidenetrazylhydrazine,



is obtained by reducing the nitrosamine of benzylamidobenzyltetrazole in alcoholic solution with zinc dust and glacial acetic acid, and treating the base with alcoholic benzaldehyde; it is also formed when benzylidenetrazylhydrazine is treated with boiling benzylic chloride. The substance is insoluble in water, and melts at 98°. *Benzylidene- β -dibenzyltetrazylhydrazine*, $\text{CHPh}\cdot\text{N}\cdot\text{N}\cdot\text{CN}(\text{CH}_2\text{Ph})_2$, is obtained by heating a solution of benzylidenetrazylhydrazine in caustic soda with benzylic chloride for several hours; it crystallises from alcohol in lustrous leaflets, and melts at 132—133°, yielding benzaldehyde when treated with boiling dilute sulphuric acid.

α -*Benzylidenetrazylhydrazine* crystallises from alcohol, and

melts at 161° ; the *hydrochloride*, which melts at 246° , is obtained as a bye-product in preparing benzylbenzylidenetetracylhydrazine. α -Benzyltetracylhydrazine is obtained by eliminating benzaldehyde from the benzylidene derivative by means of boiling hydrochloric acid; it crystallises from water in lustrous leaflets, and melts at 123° . The aqueous solution has a strongly reducing action, and yields the benzylidene derivative when treated with benzaldehyde. The *hydrochloride* crystallises in long needles, and melts and decomposes at 200° .

β -Benzylidenetetracylhydrazine is prepared by heating benzylidenetetracylhydrazine (2 grams) with sodium carbonate (1 gram), benzylic chloride (1.3 gram), and a small quantity of water and alcohol; it crystallises from alcohol and melts at 199° . Boiling mineral acids resolve the substance into benzaldehyde and β -benzyltetracylhydrazine.

α -Tribenzyltetracylhydrazine is a bye-product in the formation of benzylidene- β -dibenzyltetracylhydrazine, and also arises from treatment of tetracylhydrazine in alkaline solution with benzylic chloride; it crystallises from ethylic acetate in white needles melting at 153° , and is indifferent towards boiling dilute sulphuric acid.

β -Tribenzyltetracylhydrazine is obtained by heating benzylidenetetracylhydrazine (2 grams) with benzylic chloride (5 grams) and a 25 per cent. solution of caustic soda (10 c.c.), benzaldehyde being eliminated. It melts at 121° , and is insoluble in acids and alkalis, undergoing no change when heated with these agents. M. O. F.

Effect of Light on Diastase. By JOSEPH R. GREEN (*Ann. Agron.*, 1895, 21, 442—443; from *Annals of Bot.*, 1894, 8, 370).—Sunlight and electric light destroy diastase, the violet rays of the spectrum having the greatest effect, whilst on the other hand, the less refrangible rays have a slightly favourable effect; the colouring matter of the covering of barley thus protects the diastase from injury by light. Diastase which has been exposed to light, and afterwards kept in darkness, gradually loses its power, the destructive action induced by light continuing.

N. H. J. M.

Maltase and the Alcoholic Fermentation of Maltose. By ÉMILE BOURQUELOT (*J. Pharm.*, 1895, [6], 2, 97—105).—The question whether the enzyme, by which maltose is hydrolysed into glucose, is a chemical individual distinct from the known enzymes, such as diastase and invertase, has not yet been decided. It certainly has not been obtained in a state of purity, for the various preparations that have been made, although possessing the common property of hydrolysing maltose, differ in their powers of hydrolysing other carbohydrates; but it is hardly likely, as E. Fischer seems to suppose, that there are many maltohydrolytic enzymes differing in their powers of hydrolysing other carbohydrates, for all the well-known enzymes of this class are characterised by the limitation of their powers to the hydrolysis of single carbohydrates.

It is now fully established that there is a maltohydrolytic enzyme in the pancreas and small intestine of various animals, but the ques-

tion of the presence of such an enzyme in plants has not hitherto been investigated.

The author finds that when the common moulds, *Aspergillus niger* and *Penicillium glaucum*, are cultivated in an aqueous medium containing maltose, with tartaric acid and the usual salts, a considerable amount of the maltose is hydrolysed into glucose; and by grinding the moulds with sand, and extracting them with water, liquids can be obtained, from which a maltohydrolytic enzyme is precipitated by alcohol.

The lactic fermentation of maltose, like the alcoholic fermentation, is preceded by its hydrolysis; Fischer's isolation of glucosazone in the latter case is conclusive, and the author has proved the presence of glucose indirectly in the former case. When chloroform is added to a solution of maltose, or of a mixture of maltose and levulose, in alcoholic fermentation, the reducing power of the liquid continues to increase, whilst the rotatory power diminishes, and this can only be due to the continued formation of glucose by the hydrolytic action of an enzyme, during the suspension of the activity of the yeast.

With regard to the presence of a similar enzyme in blood, Dubourg (*Inaug. Diss.*, Paris, 1889) has proved that the blood of rabbits kept on an amylaceous diet has the power of hydrolysing maltose. It is thus clear that the assimilation of maltose in animals is always preceded by its hydrolysis into glucose.

The author inclines to the opinion that the maltohydrolytic enzyme, maltase, is a chemical individual distinct from the other well-known enzymes.

JN. W.

Preparation of Crystalline Bile acids and their Relation-ship to Colouring Matters. By RICHTER (*Chem. Centr.*, 1895, i, 282—283; from *Deut. Med. Woch.*, 1894, 21; *Vereinsbeilage*, i, 2—3).—Ox bile (250 c.c.) is treated with concentrated ferric chloride solution (10—15 c.c.), and the precipitate dissolved in sulphuric acid (60 per cent.); the residue consists chiefly of glycocholic acid; the solution, which contains the taurocholic acid, is freed from iron by means of ammonia, the filtrate diluted, sulphuric acid (10 per cent.) added until a precipitate is formed, and then shaken with ether, after 24 hours, crystals of practically pure glycocholic (? taurocholic) acid are deposited. The two acids may be separated by dissolving them in soda, and acidifying with sulphuric acid; glycocholic acid is first precipitated, and the taurocholic acid is then deposited as an oil which crystallises after some time. When these acids are treated by Hoppe-Seyler's method with ammonia and concentrated sulphuric acid, and the fluorescent product exposed to air, shaken with chloroform, and water added, a violet colour is produced; this, on further dilution, becomes deep blue, and then changes spontaneously to green. The colours are stable in the dark, but are affected by light, and their spectra resemble those of bile pigments. Human bile, and that of an ox suffering from jaundice, gave similar results, but the glycocholic acid appears to be absent.

J. B. T.

Constitution of Vegetable Proteïds. By ÉMILE C. A. FLEURENT (*Compt. rend.*, 1895, 121, 216—219).—Vegetable proteïds can be

divided into two groups, namely, those, such as gluten, casein, and vegetable fibrin, in which the ratio of ammoniacal nitrogen estimated to that calculated is greater than unity, and those, such as legumin and vegetable albumin, in which the ratio is less than unity. The fixed residue from gluten, after boiling with barium hydroxide solution (Abstr., 1894, i, 214), consists mainly of tryrosine, the caproic leucine, and the leucine, $C_6H_7NO_2$, whilst the fixed residue from legumin is a mixture of tryrosine, alanine, butalanine, and the different glucoproteins. In both animal and vegetable proteids, the water necessary for hydrolysis combines partly with special groups yielding ammonia, and carbonic, oxalic, and acetic acids, and partly with a special nucleus, yielding a fixed residue. The formula of the fixed residue from vegetable proteids, expressed in the simplest general terms, is $C_nH_{2n}N_2O_3$, whilst that from animal proteids is $C_nH_{2n}N_2O_4$. The nucleus of all the vegetable proteids examined can be represented by the general formula $C_nH_{2n-4}N_2O_3$, whilst Schützenberger found for the nucleus of egg albumin and its congeners the formula $C_nH_{2n-4}N_2O_2$. There is therefore a difference of an atom of oxygen. In both cases, as many molecules of water are necessary to hydrolysis as there are atoms of nitrogen present; in both cases also, hydrolysis takes place in two stages, and it follows that the nucleus of vegetable proteids is a mixture of imido-compounds, which are converted by hydrolysis into amido-acids. Gluten, casein, and vegetable fibrin contain a glutamine group, whilst legumin and vegetable albumin contain an asparagine group (Abstr., 1894, i, 571), and to these respectively is due the departure from unity of the ratios between the found and calculated quantities of ammoniacal nitrogen. The glutamine and asparagine groups do not exist in animal proteids, and Schützenberger has found that the quantities of ammoniacal nitrogen found and calculated are identical. These groups are the first to undergo hydrolysis, and give rise to the ammonia which is obtained by boiling gluten or legumin with alkali solutions under ordinary pressure.

C. H. B.

Albumoses. By HUGO SCHRÖTTER (*Monatsh.*, 1895, **16**, 609—618; compare Abstr., 1894, i, 215).—The method of distinguishing albumoses and peptones proposed by Kühne is valueless, since these substances and their respective salts all give precipitates with an aqueous solution of ammonium sulphate. Albumoses, however, are perfectly differentiated from peptones by their large percentage of nitrogen, by their high molecular weight, and by the still more important fact that they contain sulphur, whilst peptones contain none. The generally accepted view, that by the action of ferments or acids, albumin is first of all converted into albumoses, and finally into true peptones, is incorrect. As a matter of fact, when albumin is heated with an acid, a direct conversion into peptones, without the formation of albumoses, takes place, and this is confirmed by the fact that albumoses, when treated with an acid, are in a great measure decomposed, and give rise to no peptones.

G. T. M.

Organic Chemistry.

Action of Heat on Ethylene. By VIVIAN B. LEWES (*Proc. Roy. Soc.*, 1895, **57**, 394—404).—The apparatus and methods of analysis were the same as described in the previous paper (*Abstr.*, 1894, i, 481), except that a platinum tube was used as the decomposing chamber, and a gas combustion furnace as the source of heat. The experiments show: (1) That the initial decomposition of ethylene by heat is very rapid, but that this primary decomposition is only very slowly completed, owing to secondary reactions, which tend to re-form ethylene. Thus when only 1 in. of the platinum tube was heated, 80 per cent. of the ethylene was decomposed, and with 18 in. heated only 93·7 per cent. (2) That increase in the rate of flow of the gas through the platinum tube diminishes the decomposition when the heated area is small, but has very little effect when the heated surface is large. (3) That dilution has but little effect on the decomposition; and (4) that the decomposition of ethylene is mainly due to radiant heat. J. J. S.

Combination of Mercuric Cyanide with Bromides and with Iodides. By RAOUL VARET (*Compt. rend.*, 1895, **121**, 398—400, and 499—501; compare this vol., ii, 88 and 148).

Double Decompositions between Mercuric Cyanide and Salts of Alkali and Alkaline Earth Metals. By RAOUL VARET (*Compt. rend.*, 1895, **121**, 501—502).—Fluorides, chlorides, sulphates, nitrates, carbonates, acetates, and picrates of the metals of the alkalis or alkaline earths do not interact with mercuric cyanide. Bromides behave similarly, but there is a slight exchange of acids and bases. Iodides, on the other hand, interact, and the change is limited by the formation of salts of the type $\text{Hg}(\text{CN})_2, \text{M}''(\text{CN})_2, \text{HgI}_2$. With the sulphides there is complete double decomposition. There is more or less complete decomposition when the acid in combination with the other salt displaces (when in the free state) hydrocyanic acid from the mercuric salt; if this is not the case, there is no appreciable interaction. C. H. B.

Calcium Cyanate, a Nitrogenous Manure. By CAMILLE FAURE (*Compt. rend.*, 1895, **121**, 463).—Calcium cyanate can be prepared in large quantities in the electrical furnace, limestone and carbon being first heated at 1500°, then at 2500°, in presence of excess of nitrogen, and finally at 2500° in a current of air. C. H. B.

Alcoholates. By HENRI LESCOEUR (*Compt. rend.*, 1895, **121**, 691—692).—Solutions of sodium ethoxide in ethylic alcohol, and the products obtained by evaporation, have the following vapour pressures at 60°. Saturated solution, 138 mm.; product nearly dry, 135 mm.; product $\text{EtNaO} + 1\cdot7 \text{ EtOH}$, 60 mm.; product $\text{EtNaO} + 0\cdot8 \text{ EtOH}$,
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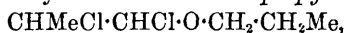
56 mm.; effloresced product, 54 mm.; almost pure EtNaO, less than 18 mm.

A compound EtNaO + 2EtOH is therefore well defined by its vapour pressure at 60°. The vapour pressure varies as follows; at 40°, 14 mm.; at 60°, 57 mm.; at 80°, 172 mm. In a dry atmosphere at the ordinary temperature, sodium ethoxide alcoholate effloresces, and yields sodium ethoxide.

Similar observations on solutions of sodium hydroxide in alcohol gave the following results at 100°. Fused product, NaOH + 3EtOH, more than 300 mm.; product partially solidified, more than 300 mm.; solid product, NaOH, EtOH, 215 mm.; effloresced product, 207 mm.; ditto, 200 mm.; almost pure NaOH, less than 30 mm. A compound NaOH + EtOH is therefore defined; its vapour pressure is 35 mm. at 76°; 207 mm. at 100°; 275 mm. at 105°. When sodium hydroxide is dissolved in boiling alcohol, and the solution is cooled, it deposits small scales, which seem to have the composition NaOH + 3EtOH; they alter very rapidly in moist air, melt easily, and give off alcohol when heated. These compounds are true alcoholates of sodium hydroxide.

C. H. B.

Action of Chlorine on Normal Propylic Alcohol. By ANDRÉ BROCHET (*Compt. rend.*, 1895, **121**, 648—650).—The action of chlorine on normal propylic alcohol in the cold results in phenomena similar to those observed with methylic and isobutylic alcohols. In the end the liquid separates into an upper layer consisting of water, hydrochloric acid, unaltered alcohol, and chloropropaldehyde, and a lower layer consisting of unsymmetrical *dichloropropylic ether*,



a colourless, very mobile liquid, with a characteristic and very persistent odour. It boils at 80° under a pressure of 15 mm., and at 176° under 762 mm.; sp. gr. at 15°/4° = 1.129; refractive index $n_D = 1.447$ at 16°. When boiled with water, the dichloropropylic ether yields a mixture of α -chloropropaldehyde and chlorodipropylic propional, $\text{CMeCl}_2 \cdot \text{CH}(\text{OPr})_2$.

α -Chloropropaldehyde, after being dried by treatment with an equal volume of sulphuric acid at -20°, is a colourless, very mobile liquid, which boils at 86° under a pressure of 755 mm.; sp. gr. at 15°/4° = 1.182°; refractive index $n_D = 1.431$ at 17°. It does not yield crystals of a polymericide in contact with sulphuric or hydrochloric acid, but there is some evidence that it very slowly polymerises in contact with a small quantity of hydrochloric acid. When oxidised with potassium permanganate, with addition of alkali, it yields acetic, carbonic, and hydrochloric acids.

Chlorodipropylic propional is obtained by the action of water or propylic alcohol on dichloropropylic ether. It is a colourless, mobile liquid, which boils at 203° under a pressure of 755 mm., and, like all acetals, is very stable; sp. gr. at 15°/4° = 0.990; refractive index $n_D = 1.430$ at 16°.

C. H. B.

Trimethylenic Glycol as a Bye-product in the Glycerol Manufacture. By ARTHUR A. NOYES and WILLARD H. WATKINS (*J. Amer.*

Chem. Soc., 1895, **17**, 890—891).—The authors have succeeded in isolating trimethylenic glycol from a specimen of glycerol of low specific gravity. This was probably formed, before saponification, by the fermentation of the glycerol present in the fat. The presence of this glycol in glycerol used for nitroglycerol manufacture might be a source of danger, owing to its violent reaction with nitric acid.

J. J. S.

Pentaglycol : a Dihydric Alcohol synthesised from Formaldehyde and Isobutaldehyde. By M. APEL and BERNHARD TOLLENS (*Annalen*, 1895, **289**, 36—46; compare Abstr., 1894, i, 353).—*Pentaglycol iodhydrin*, $\text{CH}_3\text{I}\cdot\text{CMe}_2\cdot\text{CH}_2\cdot\text{OH}$, is obtained by heating pentaglycol with hydriodic acid and phosphorus for two hours; it is a pale yellow oil, which boils at 60° in a vacuum. *Methylenepentaglycol*, $\text{C}_5\text{H}_{10}\text{<O>CH}_2$, boils at 126° .

M. O. F.

Boiling Point of Nitroglycerol. By CORNELIUS A. LOBBY DE BRUYN (*Rec. Trav. Chim.*, 1895, **14**, 131—133).—The author refers to the value obtained by Champion (*Compt. rend.*, 1871, **73**, 42) for the boiling point of nitroglycerol, and criticises the method adopted by this chemist.

A small quantity of nitroglycerol, contained in a boiling flask, was heated in a bath of glycerol to 160° , under a pressure of 15 mm., the pressure being diminished by means of a water pump. No nitroglycerol distilled over under these conditions, but the substance commenced to volatilise. The author believes that if a mercury pump had been employed, the nitroglycerol would have distilled. This negative result renders it certain that the boiling point of nitroglycerol at the ordinary temperature cannot be 185° , as stated by Champion.

Champion and Lorm have published values for the vapour pressure of nitroglycerol, according to which the boiling point of the compound would be below 200° ; these are likewise not in accord with the author's experience.

A. R. L.

Compounds of Formaldehyde with Polyhydric Alcohols. By M. SCHULZ and BERNHARD TOLLENS (*Annalen*, 1895, **289**, 20—34; compare Abstr., 1894, i, 438).—The compounds dealt with in this paper have been already described by the authors (*loc. cit.*), the class name formal being used instead of formacetal.

M. O. F.

Penta-erithrytoldibenzal. By M. APEL and BERNHARD TOLLENS (*Annalen*, 1895, **289**, 34—35; compare Abstr., 1894, i, 353).—*Dibenzylidenepenta-erithrytol*, $\text{C}_5\text{H}_8\text{O}_4(\text{C}_6\text{H}_5)_2$, melts at 160° .

M. O. F.

Anhydro-enneaheptitol from Formaldehyde and Acetone. By M. APEL and BERNHARD TOLLENS (*Annalen*, 1895, **289**, 46—51; compare Abstr., 1894, i, 353).—The authors have already described *anhydro-enneaheptitol*, $\text{OH}\cdot\text{CH}(\text{C}[\text{CH}_2\cdot\text{OH}]_3)_2$ (*loc. cit.*), and a more detailed account of the properties of the substance is now supplied.

M. O. F.

Action of Dilute Alkalis on the Carbohydrates. By CORNELIUS A. LOBBY DE BRUYN (*Rec. Trav. Chim.*, 1895, **14**, 156—165).—When a 4 per cent. aqueous solution of ordinary glucose (500 c.c.) is treated with normal potassium hydroxide solution (10 c.c.), the optical activity diminishes, until at the end of 135 hours it has sunk approximately to zero, at which it remains constant. The solution is now found to require only about one-third the calculated quantity of acid to neutralise it; the neutral solution still remains optically inactive. The same result is obtained when glucose is treated at the ordinary temperature with a more concentrated solution of potassium hydroxide; the author separated ordinary glucose from the neutralised product. Other bases, notably ammonia and barium hydroxide, behave towards glucose in the same manner. Xylose and galactose likewise undergo a change in rotatory power when treated with dilute alkalis. A. R. L.

Action of Alkalis on the Sugars. Reciprocal Transformation of Glucose, Fructose, and Mannose. By CORNELIUS A. LOBBY DE BRUYN and W. ALBERDA VAN EKENSTEIN (*Rec. Trav. Chim.*, 1895, **14**, 201—216, and *Ber.*, 1895, **28**, 3078—3082).—The optically inactive syrup which is obtained by the action of potassium or sodium hydroxide, or ammonia on glucose, is also formed by the action of calcium hydroxide, sodium, or potassium carbonate, or magnesium oxide. When, however, the action is prolonged, calcium hydroxide leads to the formation of saccharinic acid, which is not the case with potassium or sodium hydroxide (compare Kiliani, *Ber.*, 1882, **15**, 2960). The speed with which the optical activity is attained is dependent on the temperature and concentration of the solution; the most favourable temperature being 70°. Glucose (100 grams) dissolved in water (400 c.c.) and treated at this temperature with calcium hydroxide (5 grams), is transformed in a few hours. The calcium is readily precipitated by passing a current of carbonic anhydride through the solution. By this transformation, glucose is, in part, converted into mannose, which was isolated and estimated by means of its insoluble phenylhydrazone, and, in part, into fructose; a certain portion of the glucose remains unaltered, whilst another portion is converted into acids.

Fructose is also partially converted into glucose and mannose on being similarly treated with alkalis or alkaline earths, whilst mannose is, in like manner, partially converted into glucose and fructose. The authors' results are drawn up in the form of a table.

This reciprocal transformation is conditioned by a state of equilibrium which may be represented by the symbol



Actual equilibrium is never established, however, because simultaneous decomposition into acids occurs. Galactose is not formed in this reaction.

As an explanation of the mechanism of the changes which occur during this transformation, it is suggested that the two end groups in the molecule of glucose, —CH(OH)·CHO , first combine with a molecule of water, which is subsequently split off in such a manner that the

complex $\begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{CH} \cdot \text{CH} \cdot \text{OH} \end{array}$ results, which then passes, by intramolecular transposition, into the complex $\text{—CO} \cdot \text{CH}_2 \cdot \text{OH}$, which exists in the ordinarily accepted formula for fructose. By an inverse change, fructose may be assumed to give rise to the complex $\begin{array}{c} \diagup \quad \diagdown \\ \text{—CH} \cdot \text{CH} \cdot \text{OH} \\ \text{O} \end{array}$,

stereoisomeric with that above mentioned, which, by addition and loss of water, would give mannose; or the two end groups in the molecule of fructose, by addition and loss of water, may be assumed to be converted into the complex $\text{O} < \begin{array}{c} \text{CH}_2 \\ | \\ \text{CH} \cdot \text{OH} \end{array}$, which, by intramolecular transposition, may give rise to the complex $\text{—CH(OH)} \cdot \text{CHO}$.

The reciprocal transformation of the three sugars evidently plays a rôle in the chemical changes which occur in the tissues of plants. The reaction demonstrates the necessity of observing caution in drawing conclusions from experiments on the sugars made in alkaline solutions. Thus it was long thought that mannitol was the alcohol corresponding with glucose, because that alcohol is one of the products formed by reducing glucose with sodium amalgam; this was, however, disproved by E. Fischer.

The reaction also explains the fact that the technical invert sugar syrups, after the treatment with lime, are almost optically inactive, instead of being lævorotatory. An investigation of certain "foreign syrups" has shown that they contain notable quantities of mannose.

A. R. L.

Sugars richer in Carbon from Galactose. By EMIL FISCHER (*Annalen*, 1895, **288**, 139—157; compare *Abstr.*, 1890, 597).—*α-Galaheptonic acid* is the galactosecarboxylic acid obtained by Maquenne and Kiliani. Galactose (100 grams) is dissolved in warm water (150 grams) and treated at 0° with hydrogen cyanide (28 c.c.), a few drops of aqueous ammonia being also added; after remaining at 0° during 24 hours, a quantity of the amide amounting to 25 per cent. of the material employed may be removed by filtration, a further separation taking place during two following days. The amide is dissolved in boiling aqueous barium hydroxide and heated until ammonia is no longer perceptible; the hot liquid is then exactly neutralised with sulphuric acid, boiled with animal charcoal, filtered and evaporated. The syrup is then heated for several days in a porcelain basin on the water bath with successive quantities of alcohol, and by this treatment yields the lactone (*loc. cit.*), which crystallises from methylic alcohol in long needles, melting at 151° (corr.) after softening at 142°; at 20° it has the specific rotatory power $[\alpha]_D = -52.3^\circ$. The *phenylhydrazide* dissolves in 25 parts of boiling water, and crystallises in colourless, lustrous needles; it becomes brown and evolves gas at 226° (corr.) when rapidly heated.

α-Galaheptose is prepared by reducing the lactone in ice-cold solution with sodium amalgam; it is obtained as a sweet, colourless syrup on decomposing the hydrazone with benzaldehyde. The sugar

is extremely soluble in water, but dissolves with great difficulty in absolute alcohol; the aqueous solution is feebly lævorotatory, and is not fermented by yeast. The *phenylhydrazone* dissolves in 30 parts of boiling water, and crystallises in colourless needles; it evolves gas and melts at 205° (corr.). The *osazone* dissolves in 200 parts of boiling alcohol, and crystallises in yellow needles; it melts and decomposes at 224° (corr.).

α -*Galaheptitol* is obtained by reducing α -galaheptose with sodium amalgam in a solution neutralised with sulphuric acid; it crystallises in colourless needles and melts at 187 – 188° (corr.). The substance is very readily soluble in water and has a sweet taste, but dissolves with difficulty in absolute alcohol; in a concentrated solution of borax at 20° , it gave $[\alpha]_D = -4.35^{\circ}$.

Gala-octonic acid is obtained from α -galaheptose by means of hydrogen cyanide. On decomposing the amide with aqueous barium hydroxide, the *lactone* is formed, melting at 225 – 228° (corr.); at 20° it dissolves in 20 parts of water, but is scarcely soluble in absolute alcohol; the aqueous solution gives $[\alpha]_D = +64.0^{\circ}$ at 20° . The *phenylhydrazide* is colourless, and melts and decomposes at 235° (corr.); the *barium salt* is crystalline and anhydrous.

Gala-octose crystallises in colourless lustrous leaflets containing $1H_2O$, and melts at 109 – 111° (corr.); it is strongly lævorotatory. The *phenylhydrazone* crystallises in slender leaflets and melts at 205 – 210° (corr.); the *osazone* forms slender yellow needles insoluble in water, and melts at 226 – 231° (corr.).

Gala-octitol crystallises from 90 per cent. alcohol in slender needles, and from water in colourless, rectangular plates; it melts at 230 – 232° (corr.), does not reduce Fehling's solution, and is tasteless.

β -*Galaheptonic acid* is obtained from the brown mother-liquor containing the amide of the α -acid; the action of water and pyridine at 135 – 140° converts it into the α -modification. The *phenylhydrazide* dissolves in 4 parts of boiling water, and separates in colourless crystals melting at 185° ; the aqueous solution at 20° gave $[\alpha]_D = -6.32^{\circ}$.

β -*Galaheptose* crystallises in prisms and melts and decomposes at 195 – 199° (corr.); 10 minutes after preparing an aqueous solution at 20° it gave $[\alpha]_D = -22.5^{\circ}$, the final reading after 24 hours being $[\alpha]_D = -54.4^{\circ}$ at the same temperature.

The dibasic acid obtained from α -galaheptonic acid has been described by Kiliani; at 20° the aqueous solution gave $[\alpha]_D = +15.08^{\circ}$. The acid obtained from β -galaheptonic acid by oxidation with nitric acid is a syrup; the *calcium salt* contains $2H_2O$, which is lost at 130° , and the solution in hydrochloric acid is dextrorotatory.

M. O. F.

Ammonical Derivatives of Milk Sugar, Maltose, Galactose, Xylose, Arabinose, and Rhamnose. By CORNELIUS A. LOBBY DE BRUYN and FREDERIK H. VAN LEENT (*Rec. Trav. Chim.*, 1895, **14**, 134–149, and *Ber.*, 1895, **28**, 3082–3084; compare *Abstr.*, 1894, i, 221; 1895, i, 7 and 640).—Dry gaseous ammonia has no action on ordinary hydrated milk sugar, or on its anhydride at the ordinary temperature. A concentrated solution in aqueous ammonia exhibits

the normal rotation at first; the rotation diminishes, however, after some days, but the ultimate value cannot be determined on account of the darkening of the solution.

Lactose ammonia, $C_{12}H_{22}O_{11}\cdot NH_3$, an additive compound analogous to aldehyde ammonia, is obtained when ordinary hydrated milk sugar is dissolved in methyl alcoholic ammonia, and the solution concentrated after being kept for 11—18 days. It readily loses ammonia both in the dry state, and also when its aqueous solution is distilled; in the latter case about half the ammonia passes over, the remainder being retained by the coloured substances which are produced. Determinations of the molecular weight of lactose ammonia by the cryoscopic method indicate that the substance is partially dissociated in dilute solutions. The author failed to obtain salts of the compound.

Maltosamine, $C_{12}H_{21}O_{10}\cdot NH_2$, is best obtained by dissolving hydrated maltose in alcoholic ammonia; it melts and decomposes at 165° , and loses the whole of its ammonia when boiled with dilute sulphuric acid.

When galactose is dissolved in methylic alcoholic ammonia two compounds are formed:—*galactosamine ammonia*, $C_6H_{11}O_5\cdot NH_2\cdot NH_3$, which melts at 113 — 114° , and *galactosamine*, $C_6H_{11}O_5\cdot NH_2$, which melts and decomposes at 141° ; the crystals of the latter can be kept in an ordinary desiccator without losing ammonia. If either of the compounds is boiled with dilute sulphuric acid, an amount of acid is neutralised corresponding with the combined ammonia.

Xylosamine, $C_5H_9O_4\cdot NH_2$, melts and decomposes at about 130° .

Arabinosamine, $C_5H_9O_4\cdot NH_2$, melts at about 124° .

Rhamnosamine methylic alcoholate, $(C_6H_{11}O_4\cdot NH_2)_2\cdot MeOH$, is obtained by dissolving rhamnose in methylic alcohol; it may be recrystallised from methylic alcohol, and melts at about 116° , but it commences to lose ammonia below this temperature. The *ethylic alcoholate* melts at 80° with the loss of alcohol and some ammonia.

The authors have as yet failed to obtain crystalline ammoniacal derivatives from mannose and glucoheptose. A. R. L.

Action of Diastase on Isomaltose. By CARL J. LINTNER (*Chem. Centr.*, 1895, i, 91; from *Zeit. ges. Brauw.*, 1894, **17**, 378; compare this vol., i, 4).—The author has previously stated that isomaltose is readily converted by diastase into maltose. Further observations have shown that the process is not complete; in one case only 30 per cent. was changed. Experiments seem to show that isomaltose, obtained by the action of oxalic acid on starch, is not acted on at all by diastase. The author thinks that this may probably be accounted for by assuming that there are two stereoisomeric isomaltoses.

J. J. S.

Isomaltose. By EMIL FISCHER (*Ber.*, 1895, **28**, 3024—3028; compare *Abstr.*, 1891, 412, and Brown and Morris, *Trans.*, 1895, 709).—Ost (*Chem. Zeit.*, 1895, No. 67) has stated that Fischer's synthetical isomaltose is merely impure maltose; in reply, the author states that his isomaltose is quite different from maltose, as it is not fermented by yeast, nor yet by the enzymes of yeast. Isomaltosazone is best

recrystallised first from water, and, finally, several times from ethylic acetate; it cannot be obtained in the pure state by crystallisation from alcohol, the method employed by Ost. The melting point lies between 140° and 155° , according to its purity. Isomaltose, after treatment with yeast and after dialysis, yields an osazone, which melts at 158° , and has a specific rotatory power $[\alpha]_D = +7^{\circ}$. The author has not succeeded in obtaining the pure carbohydrate.

J. J. S.

Action of Heat on Starch dissolved in Glycerol. By KARL ZULKOWSKI and BOH. FRANZ (*Bied. Centr.*, 1895, **24**, 557—558; from *Ber. Oest. Ges. Förd. Chem. Ind.*, **16**, 120—127).—When pure potato starch is heated with glycerol at 190° , *soluble starch* is produced; this is precipitated by alcohol, and by lime and baryta. It changes back to ordinary starch when kept either in the dry state, or in concentrated aqueous solution. Soluble starch gives a splendid indigo coloration with iodine solution.

Erythrodextrin is formed when starch and glycerol are heated at 200° until the product gives a cherry colour with iodine; it is then precipitated with alcohol and washed with alcohol. It is a white, sandy powder, which is not hygroscopic, and is only precipitated from its aqueous solution by baryta after the addition of alcohol.

Achroodextrin is produced by heating the mixture at 210° until the product no longer gives a red colour with iodine; it is hygroscopic, and the solution is coloured distinctly brownish-yellow by extremely dilute iodine solution. When the heating at 210° is more prolonged, a product is obtained which is soluble in alcohol, but is precipitated on adding saturated baryta solution until strongly alkaline; the product consists of two substances, one a transparent, hygroscopic mass, very like gum arabic, soluble in strong alcohol, the other less transparent and hygroscopic, and soluble only in dilute alcohol.

Erythrodextrin and achroodextrin reduce distinctly, but feebly, whilst the products soluble in alcohol do not reduce at all. The rotatory power of the partially purified substances was found to be as follows:—Soluble starch, 188.3; erythrodextrin, 181.0; achroodextrin, 173.5; products soluble in dilute and in strong alcohol, 151.5 and 98.9 respectively.

N. H. J. M.

Action of Oxalic acid on Inulin. By GEORG DÜLL (*Chem. Zeit.*, 1895, **19**, 166 and 216—217).—The object of this research was to find out whether the dextrin compounds (levulins) produced during the hydrolysis of inulin with dilute sulphuric acid are really intermediate products in the inversion of the inulin into levulose, or are secondary products of reversion. The molecular weight of pure inulin was found to be 2950, which agrees with the formula, $(C_6H_{10}O_5)_{18}$, or $(C_6H_{10}O_5)_{18} + H_2O$, and the rotatory power to be $[\alpha]_D = -40^{\circ}$.

A table is given, showing the molecular weights and rotatory powers of varying mixtures of inulin and levulose.

As the result of numerous experiments made with varying quantities of oxalic acid, the author concludes that no intermediate dextrin-like substances (levulins) are formed, so that, beyond doubt, the

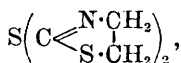
levulins produced by the action of dilute sulphuric acid on inulin are really reversion products of levulose.

Directions for preparing crystalline levulose by the action of oxalic acid on inulin are given.

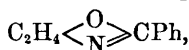
It is further shown that if oxalic acid is allowed to act on levulose for some time under pressure, a substance, $C_6H_6O_3$, which is a derivative of furfuraldehyde, is obtained. Sorbose also gives the same product (compare Kiermayer, this vol., i, 144). J. J. S.

Vinylamine. By SIEGMUND GABRIEL and ROBERT STELZNER (*Ber.*, 1895, **28**, 2929—2938; compare *Abstr.*, 1888, 668).—When bromethylamine hydrobromide, prepared by heating bromethylphthalimide with hydrogen bromide and acetic acid, is treated with 33 per cent. potash, and the resulting solution is distilled, a solution of vinylamine is obtained, from which the free base separates when solid potash is added. The base boils at $55-56^\circ$, fumes in the air, has a strongly ammoniacal smell, mixes with water, attacks the skin, and has a sp. gr. = 0.8321 at 24° . The *oxalate*, $C_2H_3N \cdot C_2H_2O_4$, forms slender needles, is readily soluble in water, and melts and decomposes at 115° .

When an aqueous solution of vinylamine is heated for some hours at 100° , the base undergoes alteration, a syrupy mass being left after evaporation, from which crystalline salts cannot be obtained. Alcohol does not produce a similar change. *Iodethyltrimethylammonium iodide*, $CH_2I \cdot CH_2 \cdot NMe_3I$, is formed by the action of methylic iodide on the base. The melting point of this substance, stated by Schmidt as $230-231^\circ$, varies with the rate at which the substance is heated. Vinylamine combines with great vigour with carbon bisulphide, thi-azoline μ -hydrosulphide, $SH \cdot C \begin{smallmatrix} \nearrow N \cdot CH_2 \\ \searrow S \cdot CH_2 \end{smallmatrix}$, being formed. This substance is converted by nitrous fumes into *thiazolyl μ -sulphide*,



which forms yellow crystals melting at $79-81^\circ$. Benzoic chloride converts vinylamine into *benzovinylamide*, $C_2H_3 \cdot NHBz$; it is an oil, which solidifies in a freezing mixture, melts a little above 0° and is partially converted by distillation into μ -phenyloxazoline,

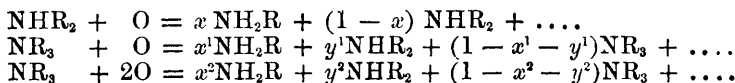


a tarry residue being left. Benzovinylamide combines very readily with the halogen acids. *Benzo- β -iodethylamide*, $CH_2I \cdot CH_2 \cdot NHBz$, crystallises in yellowish plates, and melts at 110° . Bromethylbenzamide is converted by aniline into *benzophenylethylenediamine*, $NHPh \cdot CH_2 \cdot CH_2 \cdot NHBz$, which melts at 127° . The *platinochloride* melts and decomposes at about 205° . When boiled with benzoic chloride, it is converted into *dibenzophenylethylenediamine*, melting at 147.5° . *Benzophenylpropylenediamine*, $NHPh \cdot CHMe \cdot CH_2 \cdot NHBz$, is obtained from β -bromopropylbenzamide in a similar manner. It crystallises in small needles, and melts at $110-111^\circ$.

Vinylamine unites with phenylic thiocarbimide to form vinylphenylthiocarbamide, $C_2H_3 \cdot NH \cdot CS \cdot NHPh$, which crystallises in snow-white needles, and melts at 80° . When heated with fuming hydrochloric acid at 100° , it is converted into the isomeric *n*-phenylethylene- ψ -thiocarbamide, $NHPh \cdot C \begin{smallmatrix} \nearrow N \cdot CH_2 \\ \searrow S \cdot CH_2 \end{smallmatrix}$, which forms compact, pointed prisms, and melts at 160° . Vinylphenylcarbamide, $C_2H_3 \cdot NH \cdot CO \cdot NHPh$, is formed by the combination of vinylamine with phenylic carbimide; it crystallises in compact, lustrous needles melting at $82-83^\circ$. When it is heated with hydrochloric acid, it is converted into β -chloroethylphenylcarbamide, $C_2H_4Cl \cdot NH \cdot CO \cdot NHPh$, which crystallises in colourless scales, and melts at 124° ; and this, when boiled with water, passes into *n*-phenylethylene- ψ -carbamide, $NHPh \cdot C \begin{smallmatrix} \nearrow N \cdot CH_2 \\ \searrow O \cdot CH_2 \end{smallmatrix}$, which forms colourless, vitreous needles, and melts at $119-120^\circ$. β -Chloroethylphenylcarbamide reacts in a different manner with alcoholic potash, ethylenephylcarbamide being produced. A. H.

Partial Oxidation of some Secondary and Tertiary Amines.

By R. N. DE HAAS (*Rec. Trav. Chim.*, 1895, **14**, 166—184).—The object of this research was to follow the process of oxidation of certain secondary and tertiary amines when they are treated with an insufficient quantity of different oxidising agents. The quantity of oxidising agent was so adjusted that for one molecular proportion of a secondary amine there was one equivalent of available oxygen, and for one molecular proportion of a tertiary amine there was either one or two equivalents of available oxygen. The formation of either ammonia or nitrogen was not noticed, but the reactions may be expressed by the following equations.



The author has endeavoured to determine the values of the unknown quantities x and y in these equations. The oxidising agents employed were potassium permanganate and potassium ferricyanide, and the following amines were investigated. Dimethylamine, diethylamine, dipropylamine, diisobutylamine, diamylamine, dibenzylamine, trimethylamine, triethylamine, and tripropylamine. The results are drawn up in two tables. A. R. L.

Constitution of Hexamethylenetetramine. By PAUL DUDEN and MAX SCHARFF (*Annalen*, 1895, **288**, 218—252; compare Abstr., 1895, i, 325).—Hexamethylenetetramine has been represented by numerous formulæ, and the author advocates a special expression, which consists of a symmetrically constructed tetrahedron having a nitrogen atom at each apex and a CH_2 group situated medially on each edge.

When dinitrosopentamethylenetetramine is suspended in cold water and agitated with sodium amalgam, diamidopentamethylenetetramine

is produced, but the substance has not been isolated. On adding benzaldehyde to the liquid, however, *dibenzylidenediamidopentamethylenetetramine*, $C_5H_{10}N_2(N \cdot N : CHPh)_2$, is formed; it crystallises from alcohol in long, silky needles, exhibiting feebly green fluorescence, and melts at $226-227^\circ$. Boiling concentrated alkalis are without action on the substance, but it dissolves in cold, dilute acids, giving rise to formaldehyde, ammonia, hydrazine, and benzaldehyde.

Diorthohydroxybenzylidenediamidopentamethylenetetramine is obtained by adding salicylaldehyde to a solution containing the base; it crystallises from chloroform and ether in lustrous, white needles, and melts at 213° . It dissolves in alkalis, and is resolved into formaldehyde, ammonia, hydrazine, and salicylaldehyde by warm mineral acids.

Dimetanitrobenzylidenediamidopentamethylenetetramine is obtained from metanitrobenzaldehyde and the base; it crystallises from alcohol in lustrous, golden yellow needles, and melts at 134° .

Dicinnamylidenediamidopentamethylenetetramine crystallises from alcohol in pale yellow lustrous leaflets, and melts at 207° .

Reduction of trinitrosotrimethylenetriamine with sodium amalgam gives rise to a liquid containing triamidotrimethylenetriamine. The *triorthohydroxybenzylidene* derivative of this base crystallises from a mixture of chloroform and ether in long, white needles, and melts at $139-140^\circ$.

When a freshly prepared solution of diazobenzene chloride is added to well cooled, aqueous hexamethylenetetramine, a compound, $C_{17}H_{20}N_8$, is formed, which crystallises from benzene in yellowish-brown leaflets, and melts and decomposes at 228° . It is indifferent towards boiling alkalis, but when treated with dilute acids it yields nitrogen, ammonia, aniline, and formaldehyde. No evolution of gas attends the dissolution of ice-cold concentrated hydrochloric acid, the diazobenzene residue being eliminated.

Bisparanitrodiazobenzenepentamethylenetetramine,



is obtained by mixing diazotised paranitraniline with hexamethylenetetramine at the temperature of melting ice, formaldehyde being eliminated. It dissolves with great difficulty in common solvents, but crystallises from hot ethylenic bromide in yellow needles, and melts and decomposes at 244° ; it is indifferent towards boiling alkalis, but is resolved by dilute acids into nitrogen, ammonia, paranitraniline, and formaldehyde.

Bismetanitrodiazobenzenepentamethylenetriamine crystallises from a mixture of alcohol and chloroform in lustrous, yellowish-green plates, and melts, evolving gas, at 184° ; nitrogen, ammonia, metanitraniline, and formaldehyde are formed under the influence of dilute acids.

Sodium pentamethylenetetraminebisdiazobenzenesulphonate,



is only sparingly soluble in cold, but readily in hot, water; a

portion of the water is given off at 100° , whilst above this temperature the salt becomes yellow and decomposes. The *silver* salt is amorphous, and the *copper* and *nickel* salts crystallise in minute needles; the *barium* salt, containing $3\text{H}_2\text{O}$, becomes anhydrous at 100° .

When aqueous hexamethylenetetramine is agitated with soda and benzoic chloride, two compounds are formed, one of which, dissolving in ethylenic bromide, consists of the *tribenzoyl* derivative of trimethylenetriamine; it melts at $220\text{--}221^{\circ}$, and when gently heated yields formaldehyde, ammonia, and benzoic acid. The second product, which does not dissolve in ethylenic bromide, is the *tribenzoyl* derivative of diamidodimethylamine; it crystallises in rhombohedra, and melts at $266\text{--}267^{\circ}$, yielding the same products as the foregoing substance when treated with mineral acids. M. O. F.

Reactions of Formaldehyde. By T. H. LEE (*Chem. News*, 1895, 72, 153—154).—Formaldehyde reduces permanganate immediately, and is itself oxidised to carbonic anhydride and water; it also reduces potassium ferricyanide, hot Fehling's solution, and cold alkaline mercurio-potassium iodide, although neither ammoniacal copper sulphate nor mercuric chloride is affected in this manner by it. It deepens the colour of hot ferric chloride, and the solution, after cooling and re-heating, yields with ammonia a precipitate of basic ferric formate. Formaldehyde precipitates silver from its ammoniacal solution, both in the specular and pulverulent forms.

D. A. L.

Organo-metallic Compounds. By ERNST BECKMANN and G. SCHLIEBS (*Annalen*, 1895, 289, 71—90; compare Abstr., 1892, 169).—The authors have endeavoured to ascertain the molecular weight of the sodium derivatives of certain ketones and alcohols by the ebullioscopic method. Examining camphor, menthone, deoxybenzoin, and acetophenone, dissolved in ether or benzene, they find that the sodium derivatives of these compounds appear to have molecular weights amounting to three or four times the value calculated from their empirical formulæ; the determinations are not in agreement with definite chemical expressions, being appreciably dependent on the nature of the solvent, and the authors regard it as probable that a state of equilibrium exists between the dissociating action of the solvent and the tendency to associate exhibited by the molecules of the sodium derivatives. The sodium derivative of menthol is bimolecular, whilst ethylic and isopropyl alcohols, dimethylethylcarbinol, and phenol yield compounds of simple molecular structure; the sodium derivatives of ethylic acetoacetate and ethylic malonate are also unimolecular in alcoholic solution.

The volume of hydrogen liberated on adding sodium to a solution of ethylic acetoacetate or ethylic malonate in ether is in exact agreement with the amount required by theory; when acetone is treated in this way, a quantity amounting to 4.5 per cent. of the available hydrogen is liberated (compare Freer, Abstr., 1894, i, 65).

M. O. F.

Behaviour of Thioacetic acid with Salt Solutions. By N. TARUGI (*Gazzetta*, 1895, **25**, i, 341—352; compare Schiff and Tarugi, *Abstr.*, 1895, ii, 84).—After washing with carbon bisulphide to remove free sulphur, the white precipitate obtained on adding thioacetic acid to solutions of mercuric chloride in the cold, is found to be *mercuric chlorosulphide*, $2\text{HgS}, \text{HgCl}_2$, not mercuric thioacetate as previously stated; it is an amorphous powder, soluble only in nitrohydrochloric acid. If mercuric nitrate is employed in place of the chloride, a white precipitate of *mercuric nitrosulphide*, $2\text{HgS}, \text{Hg}(\text{NO}_3)_2$, is deposited; this is a white, amorphous powder, which is blackened by soda or ammonia, and is soluble in nitrohydrochloric acid, but not in other acids. *Mercuric thioacetate*, $\text{Hg}(\text{SAC})_2$, therefore, does not seem to have been previously obtained; it may be prepared by slowly adding thioacetic acid to alcoholic mercuric acetate in the cold, when a white precipitate, immediately changing to minute, transparent, yellow crystals, is deposited. This, on washing with carbon bisulphide and crystallising from chloroform, is obtained in beautiful, white scales; it is soluble in hot benzene or chloroform, and, on treatment with concentrated nitric acid or hot hydrochloric acid, yields the nitrosulphide or nitrochloride described above, whilst, with sulphuric acid, it yields the double compound, $3\text{HgS}, \text{HgSO}_4$. The thioacetate is converted into mercuric sulphide by ammonium sulphide, or by hot potash or soda, whereas hot ammonia gives rise to the acid compound, $\text{Hg}_2\text{SH}_2\text{NOAc}$. Mercuric thioacetate is soluble in nitrohydrochloric acid, and is reduced to mercury by stannous chloride. It is accompanied in its preparation by a basic *thioacetate*, $\text{HgO}, \text{Hg}(\text{SAC})_2$, which can be separated by taking advantage of its insolubility in hot chloroform or benzene; it is a red, amorphous powder, insoluble in nitric or hydrochloric acid, but soluble in nitrohydrochloric acid.

On adding thioacetic acid to a copper salt in cold, neutral solution, a green precipitate is deposited which rapidly blackens during filtration; the filtrate slowly deposits red flocks of *cupric thioacetate*, $\text{Cu}(\text{SAC})_2$, which is not affected by air or light, is soluble in nitric acid, and is converted into the sulphide by hydrochloric acid, dilute sulphuric acid, ammonia, soda, or ammonium sulphide.

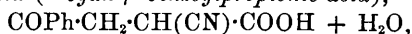
Cadmium salts in cold solution yield a precipitate of *cadmium thioacetate*, $\text{Cd}(\text{SAC})_2$, with thioacetic acid; it is a white, amorphous powder, soluble in mineral acids, and is converted into the sulphide by ammonia or ammonium sulphide.

On adding thioacetic acid to solutions of silver salts, a red precipitate is obtained which soon changes into the black silver sulphide; it is probably *silver thioacetate*.

A mixture of *lead thioacetate*, $\text{Pb}(\text{SAC})_2$, and sulphur is deposited on adding thioacetic acid to neutral lead solutions; the new salt is a white crystalline substance which is converted into the sulphate by nitric acid, and into sulphide by ammonia, soda, or ammonium sulphide. Very dilute solutions of lead chloride give, in the cold, a red precipitate of *lead chlorosulphide*, $\text{PbCl}_2, 3\text{PbS}$, from which boiling water extracts lead chloride.

W. J. P.

Synthesis by means of Ethylic Cyanacetate. By C. TIMOTHÉE KLOBB (*Compt. rend.*, 1895, **121**, 463—465).—When ethylic or methylic α -cyan- β -benzoylpropionate is mixed, in molecular proportion, with potassium hydroxide in 5 per cent. solution, and the mixture is acidified at once with sulphuric acid, and extracted with ether, *cyanphenacylacetic acid* (α -cyan- β -benzoylpropionic acid),



is obtained. It crystallises from hot water in white, nacreous plates which melt at 69°, lose their water in a dry vacuum, and then melt at 99—100°. The sodium salt crystallises with 3H₂O in prisms very soluble in water and alcohol; the silver salt is white and insoluble; the phenylhydrazine compound melts at 113°. When boiled for a long time with a large excess of potassium hydroxide, cyanphenacylacetic acid yields phenacylacetic acid, $\text{COPh}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{COOH}$, which melts at 116°, and is identical with the β -benzoylpropionic acid of Kues and Paal. *Methylic α -cyano- β -benzoyl- α -methylpropionate* forms slender needles which melt at 113°; *ethylic α -cyano- β -benzoyl- α -ethylpropionate* crystallises from carbon bisulphide in large, rhombic prisms which melt at 64°; *methylic α -cyano- β -benzoyl- α -benzylpropionate* melts at 133—134°. Attempts to displace the hydrogen by benzoyl were unsuccessful, a result analogous to that obtained by Haller with alkylic cyanacetates.

Ethylic sodiocyanacetate and chloracetone in presence of absolute alcohol, yield *ethylic cyanacetonylacete* (α -cyan- β -acetylpropionate), an amber-coloured liquid, which boils at 160—171° under a pressure of 24 mm.; sp. gr. = 1.100 at 16°. It dissolves in alkalis and in concentrated hydrochloric acid; its phenylhydrazone forms white needles which melt at 144°. Methylic sodiocyanacetate in presence of methylic alcohol yields the corresponding methyl compound which boils at 159—166° under a pressure of 26 mm.; sp. gr. = 1.148 at 16°. Its phenylhydrazone melts at 137—138°. C. H. B.

Action of Sulphur on Unsaturated Aliphatic Compounds.

By JULIUS ALTSCHUL (*Zeit. angew. Chem.*, 1895, 535—542).—The first part of this paper consists of a *résumé* of the work done by Henriques (*Chem. Zeit.*, 1893, 636), Weber (*ibid.*, 1894, 112), Anderson (*Annalen*, **63**, 370), Benedikt and Ulzer (*Monatsh.*, 1887, 208).

Saturated fatty acids, such as stearic acid, when heated with sulphur for some time a little above their melting points, are not appreciably acted on; in order to decompose such an acid, it must be heated with sulphur to at least 200°. Hydrogen sulphide is then evolved and substitution products, resembling those obtained by Benedikt, are formed. An unsaturated acid, such as oleic acid, behaves quite differently; when heated with 10 per cent. of sulphur for some time at 130—150°, complete solution ensues and chemical combination takes place without the evolution of hydrogen sulphide. All unsaturated compounds behave in exactly the same manner with sulphur, and within the same range of temperature. The author has proved that combination with sulphur does actually take place, since the products formed by the action of sulphur on fatty oils, when hydrolysed with alkali, yield soaps, and these when acidified yield acids which contain sulphur

chemically combined; the hydrolysis is best carried out at low temperatures with alcoholic potash, as when hydrolysed at fairly high temperatures, hydrogen sulphide is eliminated, and salts of acids free from sulphur are obtained (compare Henriques).

The sulphur additive compounds, just like the oxidation products, of the fats, unite with sulphur chloride, S_2Cl_2 . The fatty oils which are most readily oxidised, namely, those which most readily form additive compounds with oxygen, are also the compounds which most readily unite with sulphur. Sulphur chloride does not readily unite with those sulphur additive compounds which are difficult to prepare.

The nature of the sulphur additive compounds varies greatly with the nature of the oil and the temperature at which the operation is carried out. Oleic acid apparently unites with 1 atom of sulphur at moderate temperatures, whereas many glycerides form varying products (probably mixtures) which are largely influenced by the temperature at which the action takes place.

J. J. S.

Thiorufic and Thiocarbacetoacetic acid. By OSKAR EMMERLING (*Ber.*, 1895, **28**, 2882—2888).—The analysis and cryoscopic determination of the molecular weight of thiorufic acid lead to the formula $C_{21}H_{25}S_6O_8$, instead of the simpler formula, $C_{10}H_{14}S_3O_4$, which was ascribed to this substance by Oppenheim and Norton (*Ber.*, **10**, 701); the salts have corresponding formulæ, the sodium salt being $C_{21}H_{25}Na_4S_6O_8$. When this sodium salt is treated in the cold with aqueous soda, hydrolysis takes place, and a new acid is formed, which is very readily soluble in water, and melts at about 173° . This substance has the formula $C_{15}H_{16}S_6O_8$, and is pentabasic, the barium salt having the formula $(C_{15}H_{11}S_6O_8)_2Ba_3$. The authors propose to give the name *thiorufic acid* to this new compound, the original acid of Oppenheim and Norton being known as *etherthiorufic acid*.

Ethylic thiocarbacetoacetate was also first prepared by Oppenheim and Norton, who ascribed to it the constitution $CS:CAc:COOEt$. This formula is confirmed by the fact that when the substance is heated in alcoholic solution with lead oxide, malonic acid is formed, lead sulphide and acetic acid being also produced. Ethylic thiocarbacetoacetate yields a *dibromo-derivative*, which crystallises in thick, yellow needles, and melts at 171° , as well as a *tribromo-derivative*, which crystallises in lustrous yellow plates melting at 180° . The latter of these also yields malonic acid when it is treated with lead oxide, and this reaction proves the presence of a methyl group in the original substance. In the preparation of ethylic thiocarbacetoacetate, a small amount of ethylic malonate, which is probably derived from a partial decomposition of this compound, is always produced.

A. H.

Action of Sodium Hydroxide on Allylmalonic, Allylacetic, and Ethylidenepropionic acid. By JOHN G. SPENZER (*J. Amer. Chem. Soc.*, 1895, **17**, 1—32).—The greater part of this work has been previously published (compare Fittig and Spenser, *Abstr.*, 1895, **i**, 204). It is shown that $\gamma\delta$ -unsaturated acids behave very differently from $\beta\gamma$ -acids when boiled with sodium hydroxide solution. Allylmalonic acid is not acted on when treated in

this way, and allylacetic acid yields only a trace of an acid whose barium salt is soluble in alcohol, but the exact composition of which could not be determined. Sodium ethylenepropionate, on the other hand, is readily converted into sodium propylenacetate. In the preparation of ethylenepropionic acid by the destructive distillation of methylparaconic acid, the distillate contains valerolactone, methylcitraconic acid, methylitaconic acid, and unaltered methylparaconic acid. The author gives methods for the separation of each constituent.

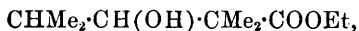
J. J. S.

Action of Zinc and Ethylic Bromisobutyrate on Acetone. Synthesis of Tetramethylethylenelactic acid. By SERGIUS REFORMATSKY and B. PLESCHONOSOFF (*Ber.*, 1895, **28**, 2838—2841).—Ethylic bromisobutyrate and acetone, in molecular proportion, are added to zinc, the mixture is cooled with water, and after a week is heated at 60—70° during two hours, water is added, the liquid is acidified with sulphuric acid, and the oil removed, washed, dried, and fractionated. The first portion consists chiefly of ethylic isobutyrate, the second portion (b. p. 150—200°) when redistilled, yields *ethylic β-hydroxytetramethylpropionate*, $\text{OH} \cdot \text{CMe}_2 \cdot \text{CMe}_2 \cdot \text{COOEt}$ (tetramethylethylenelactate), which is a thick, yellow liquid, boiling at 196—197°; it has a pleasant odour, and is insoluble in water. The free acid, prepared by hydrolysis of the ethylic salt with barium hydroxide, crystallises in plates, melts at 152—153°, previously decreasing in volume, and boils and in part decomposes at 192—193°. By the action of sulphuric acid, dimethylisopropylcarbinol and tetramethylethylene are formed; hydriodic acid yields tetramethylethyl iodide. The yield of acid is 25 per cent. of the theoretical. The *barium salt* forms stellate crystals which become pulverulent when dried. The *calcium salt* crystallises in plates, the *silver salt* in short, lustrous prisms, and the *lead salt* in tetragonal prisms; the *sodium* and *zinc salts* have also been prepared; all are readily soluble in water.

J. B. T.

Action of Zinc and Ethylic Bromisobutyrate on Isobutaldehyde. Synthesis of Secondary β-Hydroxy-acids. By SERGIUS REFORMATSKY (*Ber.*, 1895, **28**, 2842—2847).—It has been previously shown (*Abstr.*, 1887, 717) that ethylic chloracetate and zinc yield, with ketones, tertiary β-hydroxy acids, but no corresponding compounds are formed with aldehydes, the action proceeding so slowly that the latter are in part oxidised and in part undergo condensation. Ethylic bromisobutyrate reacts more quickly, and, with aldehydes, yields secondary β-hydroxy-acids. The ethylic salt and aldehyde are mixed in molecular proportion, and added to the zinc in a reflux apparatus, the flask is allowed to remain in a cold water bath during 7—9 days, then heated at 60—70° for 1—3 hours; after 24 hours, the product is treated successively with water and dilute sulphuric acid, and the oily layer removed and purified.

Ethylic β-hydroxy-α-dimethyl-β-isopropylpropionate,



is a yellow, viscid liquid with a pleasant odour, and is insoluble in water; it boils at 160° (140 mm.) and at 221—222° (738.5 mm.).

The acid crystallises in lustrous prisms, melts at 92° , and is optically inactive; at 19° , 2.03 parts dissolve in 100 of water. The yield is 58 per cent. of the theoretical. The molecular weights of both compounds were determined by the cryoscopic method in benzene. The salts are all readily soluble in water with the exception of the copper compound; the calcium salt crystallises in prisms. The acid (m. p. $111-112^{\circ}$) prepared by Hantzsch and Wohlbrück by the action of sodium on ethylic isobutyrate is diisopropyloxalic acid, not the above hydroxydimethylisopropylpropionic acid, but the latter has been previously obtained by Fosseck by oxidising the aldol condensation product of isobutaldehyde. When distilled with dilute sulphuric acid (1 : 5), the above acid yields carbonic anhydride, dimethylisopropylethylene, and a neutral compound, which is probably a lactone, $\text{CMe}_2\text{-CO}$
 $\text{CH}_2\text{CMe}_2 > \text{O}$; it boils at $209-211^{\circ}$, melts at $52.5-53.5^{\circ}$, and its formation is probably preceded by that of the unsaturated $\beta\gamma$ -acid. By the action of hydriodic acid on the propionic acid, the same lactone is formed together with heptylic iodide (?) in small quantity.

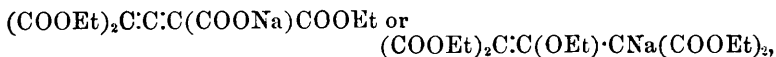
J. B. T.

Formation of Carbon Chains. II. Conjugated Ethereal Malonates. By CARL A. BISCHOFF (*Ber.*, 1895, 28, 2824-2835; compare this vol., i, 84).—Hitherto only compounds of the types
 $\overset{1}{\text{CO}}\cdot\overset{2}{\text{CX}}\cdot\overset{3}{\text{C}}\cdot\overset{4}{\text{CX}}\overset{5}{\text{CO}}$; $\overset{1}{\text{CO}}\cdot\overset{2}{\text{CX}}\cdot\overset{3}{\text{C}}\cdot\overset{4}{\text{C}}\cdot\overset{5}{\text{CX}}\cdot\overset{6}{\text{CO}}$; $\overset{1}{\text{CO}}\cdot\overset{2}{\text{CX}}\cdot\overset{3}{\text{C}}\cdot\overset{4}{\text{C}}\cdot\overset{5}{\text{C}}\cdot\overset{6}{\text{CX}}\cdot\overset{7}{\text{CO}}$
 $\begin{array}{ccccc} \text{CO} & \text{CO} & & \text{CO} & \text{CO} \\ | & | & & | & | \\ 5 & 1 & & 6 & 1 \end{array}$; have

been prepared from ethylic alkylsodiummalonates and methylenic iodide, ethylenic bromide, and trimethylenic bromide respectively. The difficulty of obtaining methylenic bromide in quantity has, for the present, restricted the quantitative investigation of the reaction to the second and third type; the results are in complete accord with the dynamical theory which indicates that the linking should be effected more readily in the latter (position 1-7) than in the former (position 1-6) case.

(1) *Ethylenic bromide with ethylic alkylmalonates.*—The malonate was mixed with alcoholic sodium ethoxide, and ethylenic bromide added; after boiling during 10 hours more ethylenic bromide was added, the boiling continued during seven hours, and this treatment repeated until the liquid was no longer alkaline. The normal compound was never formed in any considerable quantity, the products being mixtures of the original ethylic salt and the bromo-derivative, $\text{CX}(\text{COOEt})_2\text{CH}_2\text{CH}_2\text{Br}$. A portion of the ethylic salts undergo hydrolysis, and the sodium derivatives thus formed dissolve in the crude product and decompose during the distillation, forming gaseous substances; this was most marked in the case of ethylic isobutylmalonate. The following ethylic alkylmalonates were employed: Methyl-, ethyl-, propyl-, isopropyl-, isobutyl-, isoamyl-, and allyl-. Experiments were also made with mono-, di-, and tri-methylethylenic bromides; in no case is the reaction normal, but, with trimethylethylenic bromide, for example, the ethylic malonates combine, and trimethylethylene is formed.

(2) *Trimethylenic bromide with ethylic sodiomalonate and ethylic sodiomethylmalonate respectively.*—In both these cases, normal products were obtained and identified by analysis and observation of their boiling point. The substitution of allylic tribromide for trimethylenic bromide gives rise to abnormal products. From carbon tetrachloride and ethylic sodiomalonate, a compound containing only two malonyl radicles was obtained. Chabrié has described a compound with four radicles, $C[CH(COOEt)_2]_4$, but a repetition of his experiments does not confirm the statement; ethylic ethanetetra-carboxylate and an orange-yellow sodium compound.

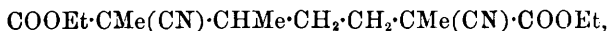


are formed (compare Zelinsky and Doroschewsky, Abstr., 1895, i, 129).

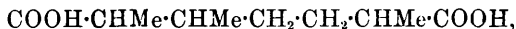
Experiments with ethylic sodio- and disodio-malonate and tetrachloro-, and tetraiodoethylene show that the action proceeds according to the equation $4CHNa(COOEt)_2 + C_2I_4 = 4NaI + C_2H_2 + CH(COOEt)_2 \cdot CH(COOEt)_2 + C(COOEt)_2 \cdot C(COOEt)_2$; the quantity of acetylene formed is practically the same from both the sodium compounds, and is about twice as great as from an equivalent quantity of sodium ethoxide; the substitution of xylene for alcohol as the solvent has little influence on the reaction. Negative results were obtained with the two sodium compounds and hexachlorethane and hexachlorobenzene. Full experimental details are given in the paper.

J. B. T.

Trimethylpimelic acid. By NICOLAI D. ZELINSKY and A. REFORMATZKY (*Ber.*, 1895, 28, 2943—2945).—A mixture of ethylic cyanopropionate and dibromobutane, $CHMeBr \cdot CH_2 \cdot CH_2Br$ (Demjanow, Abstr., 1895, i, 191), was treated with sodium ethoxide; the resulting ethylic dicyanotrimethylpimelate,



boils at 232—233° under 20 mm. pressure. When it is boiled with sulphuric acid, it becomes hydrolysed, and loses carbonic anhydride, and trimethylpimelic acid,



is obtained; this boils at 213—215° under 15 mm. pressure. When the calcium salt is distilled with excess of calcium hydroxide, that fraction of the distillate which boils at 190—191° consists mainly of trimethylketohexamethylene, $CH_2 < \begin{smallmatrix} CHMe \cdot CHMe \\ CH_2 - CHMe \end{smallmatrix} > CO$. This has a sp. gr. = 0.9129 at 18°/4°, and smells of peppermint; in moist ethereal solution, it is reduced by sodium to the alcohol, which boils at 193—195° under 747 mm. pressure, has a sp. gr. = 0.9119 at 17°/4°, and smells like menthol.

C. F. B.

Alloisomerism. By ARTHUR MICHAEL (*J. pr. Chem.*, 1895, [2], 52, 289—325; compare Abstr., 1891, 1184; 1893, i, 142, 144).—

This, and the four succeeding papers, are devoted to the exposition of facts and theories which are at variance with van't Hoff's stereochemical hypothesis and with Wislicenus's arguments in support thereof.

The best methods for obtaining bromine additive compounds of unsaturated acids are dealt with. *Citradibromopyrotartaric anhydride*, $C_3H_4Br_2O_3$, is a yellowish oil, and is prepared by exposing a mixture of the calculated quantities of citraconic anhydride and bromine to sunlight.

Bromomaleïc acid was prepared by three methods, each of which is described, and was found to be identical in each case, and Petri's conclusion with respect to Kekulé's results (Abstr., 1879, 373) is confirmed; the acid melts at $136-138^\circ$, not 128° (*loc. cit.*). A similar investigation into the methods for preparing bromofumaric acid led to a similar conclusion; the acid melts at $185-186^\circ$, not $177-178^\circ$. Details of the behaviour of the lead and silver salts of both these acids are given. By taking advantage of the difference in solubility of the hydrogen potassium salts of these acids (100 parts of water at 14° dissolve 4.04 parts of the bromofumarate and 23.8 parts of the bromomaleate), it was shown that when dibromosuccinic acid is boiled with water (*loc. cit.*), about 2-3 per cent. of bromofumaric acid is produced, together with bromomaleïc acid, but the converse production of bromomaleïc acid together with bromofumaric acid, when isobromosuccinic acid is boiled with water, could not be proved.

According to the generally accepted configuration for bromomaleïc and bromofumaric acids, the former should lose hydrogen bromide more readily than the latter, these elements being plane-symmetrical in bromomaleïc acid; experiments were accordingly made with chloromaleïc and chlorofumaric acids, in which equal weights were treated with a slight excess of caustic potash under the same conditions, and the amount of potassium chloride formed was determined in each case after the lapse of a certain time. It was found that at 10° , in the course of 48 hours, about 48 times as much hydrogen chloride was eliminated from chlorofumaric acid as from chloromaleïc acid under similar conditions; even at 100° , this difference is still to be noticed after the lapse of 15 minutes, the ratio of decomposability being, however, much smaller, namely, 1 : 1.2 instead of 1 : 48. In the same way, it was shown that in the course of 24 hours at 10° , bromofumaric acid lost 18 times as much hydrogen bromide as bromomaleïc acid did. If the facility with which halogen hydride is eliminated from these acids is to be regarded as indicative of plane-symmetry of structure, then the above experiments show that bromofumaric acid is plane-symmetrical.

Another argument advanced by Wislicenus for plane-symmetry in an acid is that such a configuration must be indicated by easy elimination of carbonic anhydride from the salts of the acid. Accordingly, a comparison was made between the amount of carbonic anhydride lost by equal weights of silver bromofumarate and silver bromomaleate respectively, when heated at 100° in aqueous solution, and it was found that in two hours silver bromomaleate lost 4.3 times as much carbonic anhydride as silver bromofumarate did. When the

same method was applied to silver bromomesaconate and silver bromocitraconate, it was found that in 16 hours at 105° the bromomesaconate had lost 3.68 per cent. of carbonic anhydride, and the bromocitraconate 7.11 per cent.

Bromomaleic acid yields fumaric acid when reduced by zinc dust, even in absence of alkalis, which are known to partially convert maleic into fumaric acid; so, also, bromocitraconic acid yields mesaconic acid, even in the absence of alkalis.

Bandrowski's statement (*Ber.*, 1882, 15, 2695) that chlorofumaric acid is obtained when hydrogen chloride reacts with acetylenedicarboxylic acid is confirmed; this is contrary to Wislicenus's interpretation of van't Hoff's hypothesis.

By adding a strong solution of potassium thiocyanate to one of maleic acid, fumaric acid is precipitated; but this conversion does not admit of a similar interpretation to that applied by Wislicenus to the conversion effected by mineral acids (*Räuml. Anord.*, 29). Isodibromosuccinic acid is converted into dibromosuccinic acid when heated with a saturated solution of hydrogen bromide at 100° in a sealed tube.

A. G. B.

Relative Ease of Elimination of Carbonic Anhydride from the Silver Salts of the β -Chlorocrotonic acids. By ARTHUR MICHAEL and T. H. CLARK (*J. pr. Chem.*, 1895, [2], 52, 326—330).—Silver β -chlorallocrotonate is decomposed with elimination of carbonic anhydride more easily than is silver β -chlorocrotonate. β -Chlorallocrotonic acid yields β -chlorocrotonic acid when heated with hydrochloric acid. Ethylic dibromofumarate loses halogen more easily than ethylic dibromomaleate does.

A. G. B.

Allomerism. By ARTHUR MICHAEL and GEORG TISSOT (*J. pr. Chem.*, 1895, [2], 52, 331—343).—It has been shown already (*Abstr.*, 1893, i, 142) that dichlorosuccinic acid yields chlorofumaric acid when it loses hydrogen chloride; when heated with acetic anhydride, however, it yields chloromaleic acid, and this, by reduction with zinc, is converted into fumaric acid. When sodium dichlorosuccinate is heated in aqueous solution for half an hour, it is converted into sodium chloromaleate, a result which renders it possible that when excess of alkali is used (*loc. cit.*), the production of chlorofumaric acid is due to the further action of this alkali on chloromaleic acid.

Dichlorosuccinic acid yields both racemic acid and inactive tartaric acid when its halogen atoms are replaced by hydroxyl groups, in this resembling dibromosuccinic acid.

Bromomesaconic acid (*Abstr.*, 1894, i, 444) melts at 217—218°, and dissolves easily in water, alcohol, acetic acid, and ethylic acetate, but only very sparingly in benzene and chloroform.

Mesadichloropyrotartaric acid yields the same products when heated with water as are obtained from citradichloropyrotartaric acid under the same conditions (*Abstr.*, 1893, i, 142). Citradichloropyrotartaric acid does not yield the so-called hydroxycitraconic acid when heated with baryta water (Morawski, *J. pr. Chem.*, [2], 11, 446).

The behaviour of xeronic anhydride and of aconitic acid and its

ethereal salts towards halogens was studied, without any very definite results.

A. G. B.

The Laws of Alloisomerism and their Employment in Classifying Unsaturated Organic Compounds. By ARTHUR MICHAEL (*J. pr. Chem.*, 1895, [2], 52, 344—365.—The following rules constitute a summary of the modes of formation, reactions, and stability of alloisomeric compounds as elucidated by the experiments of the author and his fellow-workers.

1. If two unsaturated monohalogen acids are obtainable from one saturated $\alpha\beta$ -dihalogen acid, they will be alloisomeric α -derivatives.

2. The maleinoid modifications of unsaturated compounds are more easily soluble, of lower melting point, and more volatile than the corresponding fumaroid modifications.

3. Of two halogen-free, alloisomeric, unsaturated acids, that of lower melting point will be converted into the fumaroid modification, of higher melting point, by being heated with water, mineral acids, or halogens.

4. The lower melting, maleinoid form of an $\alpha\beta$ -unsaturated α -halogen acid passes into the higher melting, fumaroid form when heated, and when under the influence of mineral acids.

5. Fumaroid derivatives from $\alpha\beta$ -unsaturated halogen-free monobasic acids of the ethylene series, formed by the replacement of β -hydrogen by a negative atom or radicle (halogen or carboxyl), are converted by heat, either entirely or in part, into the corresponding maleinoid modifications.

6. The maleinoid modifications referred to in 5, are converted, entirely or partly, into the fumaroid modifications when heated with mineral acids.

7. If the halogen is present in the α - as well as in the β -position in alloisomeric $\alpha\beta$ -unsaturated ethylene compounds, the influence of each position is exerted, and such compounds are partially converted into each other when heated.

8. The addition of 1 mol. of halogen hydride to an $\alpha\beta$ -unsaturated acid of the acetylene series directly produces, either entirely or in great part, a β -halogen acid of the higher melting fumaroid form.

9. The higher melting, fumaroid modification of two alloisomeric, $\alpha\beta$ -unsaturated, α - or β -halogen acids of the acetylene series yields halogen hydride more easily than does the lower melting maleinoid modification.

10. A mixture of two alloisomeric additive products is formed when bromine is added to an acetylene derivative containing a negative radicle in the place of hydrogen, but the fumaroid modification will be directly formed in the larger proportion.

11. Of two alloisomeric $\alpha\beta$ -dibromomethylene derivatives, the fumaroid modification yields a halogen-free acetylene derivative by loss of bromine more easily than the maleinoid modification does.

12. By the addition of bromine to both modifications of an $\alpha\beta$ -unsaturated α -bromo-acid, the same unsaturated tribromo-acid is obtained.

13. Both alloisomeric modifications of an $\alpha\beta$ -unsaturated α -halogen

fatty acid yield wholly, or in great part, the same halogen-free acid, namely, the higher melting fumaroid modification, when the halogen is replaced by hydrogen.

14. The silver salts of alloisomeric, $\alpha\beta$ -unsaturated β -halogen acids of the ethylene series are decomposed by water with formation of silver acetylide, or silver alkylacetylide, carbonic anhydride, and silver haloid. This decomposition takes place more readily in the case of a maleinoid form than in the case of a fumaroid form.

15. By separation of halogen from the two modifications of a saturated $\alpha\beta$ -dihalogen acid or its ethereal salt, the fumaroid modification of the corresponding unsaturated acid, or its ethereal salt, is formed.

16. By the elimination of 1 mol. of hydrogen bromide from the product of the addition of bromine to a fumaroid fatty acid of the ethylene series, there is produced, for the major part, a maleinoid α -bromo-acid; contrariwise, a fumaroid bromo-acid is the chief product of a similar change in an allo- $\alpha\beta$ -dibromo-acid. In the case of the corresponding chloro-acids, the elimination of hydrogen chloride yields a mixture of both α -chloro-acids.

17. No generalisation is yet possible concerning the stability of saturated alloisomeric $\alpha\beta$ -dibromo-fatty acids towards mineral acids.

18. Chlorine and bromine are not necessarily equivalent elements in an alloisomeric sense, so that the behaviour of a chlorinated derivative cannot be deduced from that of a brominated derivative.

19. Ring-formation is a periodic function of the chain-length.

20. The relative positiveness and negativeness of an unsaturated carbon atom is dependent on its absolute distance from the other atoms of the molecule, so that the "positive-negative rule" (Abstr., 1889, 1140) is applicable for the ascertainment of the position of such atoms.

A table of maleinoid and fumaroid modifications of $\alpha\beta$ -unsaturated alloisomeric compounds is given, together with detailed examples of the foregoing rules.

The untenable character of the Wislicenus-van't Hoff configuration is then discussed.

A. G. B.

Alloisomerism: Remarks on the Work of Bischoff, Wislicenus, and van't Hoff. By ARTHUR MICHAEL (*J. pr. Chem.*, 1895, [2], 52, 365—372).—A controversial paper.

Influence of Substitution on the Course of the Reactions of Ketones. By PAVEL IW. PETRENKO-KRITSCHENKO, L. PISSARSCHEWSKY, and M. HERSCHKOWITSCH (*Annalen*, 1895, 289, 52—58).—In view of the attention which has been recently directed to the influence of substitution on chemical behaviour, the authors have investigated the action of phosphorus pentachloride on alkylic salts of substituted acetonedicarboxylic acids. It has been shown by von Pechmann, that towards this agent ethylic acetonedicarboxylate exhibits the behaviour of alkylic salts of normal ketonic acids, and the authors have found that the ethylic salts of mono- and di-methylacetonedicarboxylic acids, and of mono- and di-ethylacetonedicarboxylic acids

are also vigorously attacked by phosphorous pentachloride. This agent acts on ethylic trimethylacetonedicarboxylate, whilst ethylic triethylacetonedicarboxylate is indifferent towards it, this difference in behaviour being due to the respective masses of the substituents.

Ethylic tetramethylacetonedicarboxylate boils at 146—152°, under a pressure of 25 mm.; it is indifferent towards phosphorus pentachloride, which has no action on ethylic tetrethylacetonedicarboxylate.

Whilst the behaviour of ethylic acetoacetate towards phosphorus pentachloride is normal, derivatives containing one or two alkyl substituents undergo chlorination.

M. O. F.

Influence of Substitution on the Course of the Reactions of Ketones. By PAVEL IW. PETRENKO-KRITSCHENKO and S. EPHRUSSI (*Annalen*, 1895, **289**, 58--61; compare the foregoing abstract).—Generation of heat marks the combination of phenylhydrazine with ethylic monomethylacetonedicarboxylate and ethylic monethylacetonedicarboxylate, action being less energetic in the case of the latter salt. The *hydrazone* of ethylic monomethylacetonedicarboxylate crystallises from dilute alcohol in lustrous plates, and melts at 129—130°; when hydrolysed with caustic soda, it yields the *hydrazone* of the acid, which melts and evolves carbonic anhydride at 168—169°, yielding a pyrazolone derivative.

M. O. F.

Action of Carbon Tetrachloride on Methylic Sodiomalonate. By NICOLAI D. ZELINSKI and A. PORCHUNOW (*Ber.*, 1895, **28**, 2946—2947).—When carbon tetrachloride acts on methylic sodiomalonate, $\text{CHNa}(\text{COOMe})_2$, in the presence of sodium methoxide, a substance is formed which melts at 136—137°. It appears to have the composition $\text{OH}\cdot\text{C}[\text{CH}(\text{COOMe})_2]_3$.

C. F. B.

Dihydroxytrimethylglutaric acid. By NICOLAI D. ZELINSKI and L. TSCHUGAEW (*Ber.*, 1895, **28**, 2940—2942).—Methyl acetylacetone, $\text{CHMe}(\text{CMeO})_2$ (Dunstan and Dymond, *Trans.*, 1891, 428), was converted by means of hydrocyanic acid into a *nitrile*, which yielded *dihydroxytrimethylglutaric acid*, $\text{CHMe}[\text{CMe}(\text{OH})\cdot\text{COOH}]_2$, when hydrolysed with hydrochloric acid in the cold. The nitrile melts at 124—125°. The acid melts at 83—84°, and easily loses 1 mol. of water, forming a *lactonic acid*, which melts at 119—120°; when distilled under atmospheric pressure, it yields a solid *dilactone*. It is remarkable that the lactonic acid very readily unites with water, re-forming the dihydroxy-acid.

C. F. B.

Isopropylglutolactonic acid; Constitution of Terpenylic acid. By RUDOLPH FITTIG and ADOLF WOLFF (*Annalen*, 1895, **288**, 176—191).—The authors' investigation having shown that isopropylglutolactonic acid, $\text{CHMe}_2\cdot\text{C}(\text{COOH}) < \text{CH}_2\text{CH}_2 > \text{CO}$, bears no resemblance to terpenylic acid, the constitution of the latter substance is probably represented by the formula $\text{O}\cdot\text{CMe}_2 > \text{CH}\cdot\text{CH}_2\cdot\text{COOH}$, an

expression which was first advocated by Wallach, and has been recently supported by Schryver.

β-1-Dibromisheptonic acid, $\text{CHMe}_2\cdot\text{CHBr}\cdot\text{CHBr}\cdot\text{CH}_2\cdot\text{COOH}$, is obtained by adding bromine to a solution of *β*-γ-isheptenic acid in carbon bisulphide, the operation being carried on in diffused daylight at 0° in absence of moisture; it melts at 102–103°, and crystallises in transparent, colourless plates belonging to the monosymmetric system, $a : b : c = 0.732 : 1 : 0.641$; $\beta = 67^\circ 15'$. When heated during 24 hours with water in a reflux apparatus, the acid is converted into isheptenolactone and hydroxyisheptolactone (Abstr., 1895, i, 207), *δ*-dimethyllevulinic acid being formed at the same time (*loc. cit.*); the *calcium* salt of this acid contains $3\frac{1}{2}\text{H}_2\text{O}$, and the *silver* salt is indifferent towards light.

Isopropylglutolactanic acid is obtained by adding a concentrated solution of *δ*-dimethyllevulinic acid to finely powdered potassium cyanide, allowing the mixture to remain at the ordinary temperature during 24 hours, and adding concentrated hydrochloric acid while the liquid is kept cool with ice; it melts at 67–68°. The acid separates from a mixture of ether and petroleum in small, monosymmetric crystals; it is very soluble in water, but does not crystallise from the aqueous solution. The *barium* salt contains $2\text{H}_2\text{O}$, and crystallises in monosymmetric prisms; the *calcium* salt contains $2\frac{1}{2}\text{H}_2\text{O}$, and the *silver* salt is indifferent towards light and heat. The *amide* is an intermediate product formed in hydrolysing the cyanhydrin with hydrochloric acid; it crystallises from water in lustrous, transparent prisms belonging to the monosymmetric system; $a : b : c = 0.7771 : 1 : 0.76382$; $\beta = 54^\circ 34'$.

When isopropylglutolactonic acid is heated with aqueous alkalis, salts of isopropylhydroxyglutaric acid are produced. The *barium* salt is anhydrous; the *calcium* salt contains $3\text{H}_2\text{O}$, and the *silver* salt is amorphous.

M. O. F.

Aconitic acid from *Adonis vernalis*. By N. ORLOFF (*Chem. Centr.*, 1895, i, 202; from *Pharm. Zeit. Russ.*, **33**, 771).—*Adonis vernalis* gives better yields than either *Aconitum* or *Equisetum*. After several drops of concentrated lead acetate solution have been added to the aqueous extract, and the precipitate formed has been removed, excess of the reagent is added, and the precipitate collected, well washed, and decomposed by dilute sulphuric acid. The filtrate is concentrated, and extracted with ether; after evaporation of the ether, the aqueous solution of aconitic acid is decolorised by means of animal charcoal.

J. J. S.

Formation of Citric acid by the Oxidation of Cane Sugar. By EDWIN F. HICKS (*Chem. News*, 1895, **72**, 165–166).—Phipson dissolved a few grams of cane sugar in water, to which a few drops of sulphuric acid had been added, and poured in a rather strong solution of potassium permanganate; in a short time, at summer temperature, the solution became clear and colourless. When this was neutralised with ammonia and calcium chloride added, there was no precipitate in the cold, but, on heating, crystalline calcium citrate

separated; with large quantities of permanganate, oxalic acid was also produced.

The author of the present note has repeated and also varied the experiment, using acid above and below 1 per cent.; with the former a precipitate is obtained both in cold and hot solution, but with the latter, only in the hot solution, the precipitate in all cases being calcium sulphate without a trace of organic acid. When nitric acid was used instead of sulphuric acid, no precipitate was obtained.

D. A. L.

Citric and Tartaric acids from Cane Sugar. By THOMAS J. PHIPSON (*Chem. News*, 1895, **72**, 190—191 and 257).—The failure of others to obtain citric acid from cane sugar (compare preceding abstract) is attributed by the author to the use of insufficient permanganate, of which a quantity not less than the weight of the sugar should be used; temperature and the character of the acid used are also stated to play an important part. Moreover, he finds that when a solution of equal weights of sugar, nitric acid, and potassium permanganate, after being left for 24 hours in the cold, is neutralised with calcium carbonate, a copious precipitate containing calcium tartrate is obtained, and the clear solution, on boiling, yields a further precipitate, which is calcium citrate. Saccharic acid and formic acid have also been obtained in these reactions by the author.

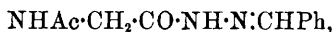
D. A. L.

Citric acid from Cane Sugar. By ALFRED B. SEARLE and ARNOLD R. TANKARD (*Chem. News*, 1895, **72**, 235, 268).—Hicks' (see above) results confirm previous work of the authors, who have since endeavoured to obtain citric acid in accordance with the method set forth by Phipson (preceding abstract), using equal weights of cane sugar, nitric acid (sp. gr. 1.42), and permanganate, the latter being added in strong solution. They did not obtain citric acid, but when sulphuric acid was used instead of the nitric acid, calcium sulphate was obtained as in their previous experiments.

D. A. L.

Hydrazides of Substituted Amido-acids; Fumarylhydrazide. By RUDOLF RADENHAUSEN (*J. pr. Chem.*, 1895, [2], **52**, 433—454).—The method adopted for the preparation of ethylic salts of substituted amido-acids containing an acid radicle consists in warming ethylic amidoacetate hydrochloride with an acid anhydride and anhydrous sodium carbonate, the change occurring in the sense of the equation $2\text{NH}_2\cdot\text{CH}_2\cdot\text{COOEt}\cdot\text{HCl} + (\text{R}\cdot\text{CO})_2\text{O} + \text{Na}_2\text{CO}_3 = 2\text{R}\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{COOEt} + 2\text{NaCl} + 2\text{H}_2\text{O} + \text{CO}_2$. An acidic chloride may be substituted for the anhydride, but if the sodium carbonate is omitted, the yield is very small. In this way, ethylic hippurate, ethylic acetylamidoacetate, ethylic succinylamidoacetate, and ethylic phthalylamidoacetate have been prepared, and details of the necessary operations are given. Ethylic succinylamidoacetate was prepared by Haller and Arth, who named it ethylic succinimidoacetate (*Abstr.*, 1887, 1031); the author ascribes to it the formula $\begin{array}{c} \text{C}_2\text{H}_4\cdot\text{C}\cdot\text{N}\cdot\text{CH}_2\cdot\text{COOEt} \\ \text{CO}-\text{O} \end{array}$, and a similar constitution to ethylic phthalylamidoacetate.

Acetamidoacetohydrazide, $\text{NHAc}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{NH}_2$, is prepared by mixing the calculated quantities of ethylic acetamidoacetate and hydrazine hydrate, alcohol and water being eliminated; it forms long, prismatic crystals, melts at 115° , and dissolves fairly easily in alcohol and water, but not in ether. During its preparation some *diacetamidoacetohydrazide*, $(\text{NHAc}\cdot\text{CH}_2\cdot\text{CO})_2\text{N}_2\text{H}_2$, is formed, and remains undissolved by alcohol; this compound is a white, crystalline powder, which is somewhat soluble in water, and melts and decomposes at 250° . *Benzylideneacetamidoacetohydrazide*,



from acetamidoacetohydrazide and benzaldehyde, crystallises in lustrous laminae, melts at 198° , and dissolves in alcohol. With nitrous acid, acetamidoacetohydrazide yields a white compound, which probably consists in part of the corresponding azide, but readily breaks up, with elimination of nitrogen and the formation of a compound which is regarded as *acetamidoacetylcarbanil*,

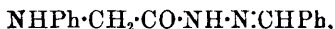


the investigation of this compound is not yet completed.

The reaction between ethylic succinamidoacetate and hydrazine hydrate does not yield the corresponding hydrazide, but a compound, $\text{C}_8\text{H}_{16}\text{N}_6\text{O}_4$, which forms colourless crystals and dissolves freely in water, but only sparingly in alcohol; it forms a white condensation product with benzaldehyde, and may therefore be supposed to contain the group $(\text{N}\cdot\text{NH}_2)''$ or $(\text{NH}\cdot\text{NH}_2)'$.

Ethylic phthalylamidoacetate yields phthalylhydrazide (Abstr., 1895, i, 354) when treated with hydrazine hydrate.

Ethylic phenylamidoacetate and hydrazine hydrate yield *phenylamidoacetohydrazide*, $\text{NPh}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{NH}_2$, which crystallises in large, transparent tables, melts at 126.5° , and dissolves freely in warm alcohol and water, but only sparingly in ether; it reduces Fehling's solution. *Benzylidenephénylamidoacetohydrazide*,



crystallises in white needles and melts at 176° . *Isopropylidenephénylamidoacetohydrazide*, $\text{NPh}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{N}:\text{CMe}_2$, crystallises in white needles and melts at 183° .

Nitrosophénylamidoacetylazoimide, $\text{NO}\cdot\text{NPh}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{N}_3$, is formed, together with nitrosodiphenylamine, when phenylamidoacetohydrazide (1 mol.) is treated in the cold with sodium nitrite (2 mols.) and glacial acetic acid; it crystallises in slender, yellow needles, melts at $41\text{--}42^\circ$, and dissolves in cold alcohol, ether, benzene, and acetone, but not in water.

Fumarylhydrazide, $\text{C}_2\text{H}_2(\text{CO}\cdot\text{NH}\cdot\text{NH}_2)_2$, is prepared from dimethylic fumarate and hydrazine hydrate; it crystallises in lustrous, colourless laminae, becomes yellow at 200° , melts and decomposes at 220° , and dissolves somewhat freely in hot water, very sparingly in alcohol, and not at all in ether.

Isopropylidenefumarylhydrazide, $\text{C}_2\text{H}_2(\text{CO}\cdot\text{NH}\cdot\text{N}:\text{CMe}_2)_2$, forms white crystals and melts at 220° ; when treated with benzaldehyde, it yields

the corresponding *benzylidene* derivative, $C_2H_2(CO \cdot NH \cdot N : CHPh)_2$, which crystallises in white laminæ and decomposes at about 220° .

Fumarylazoinide, $C_2H_2(CO \cdot N_3)_2$, has been prepared in the usual manner as a colourless, crystalline compound, but it explodes when dried. By heating it with absolute alcohol, nitrogen is eliminated, and *ethylic fumarylcarbamate*, $C_2H_2(NH \cdot COOEt)_2$, is obtained; this forms small, yellow needles, which become dark when heated, and melt and decompose at 220° ; it is a neutral compound, and dissolves freely in water, alcohol, ether, acids, and alkalis. A. G. B.

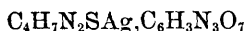
Optically Active Halogen Compounds. By PAUL WALDEN (*Ber.*, 1895, 28, 2766—2773).—The author replies to Le Bel's criticisms (*Abstr.*, 1895, i, 585) on his previous work (*Abstr.*, 1895, i, 450).

On treating Fileti's *d*-isopropylphenylglycollic acid with phosphorus pentachloride, inactive chlorisopropylphenylacetic acid, melting at 82° , was obtained, but by operating more carefully with *l*-isopropylphenylglycollic acid, a *dextrochlorisopropylphenylacetic acid*, melting at 75 — 76° , and having the specific rotation $[\alpha]_D = +23.3^\circ$ in a 3 per cent. benzene solution, was isolated; evidently the active glycollic acid very readily becomes racemic when the hydroxyl group is exchanged for chlorine.

On brominating asparagine by passing nitric oxide through its dilute sulphuric acid solution containing potassium bromide and bromine, *lævobromosuccinamic acid*, $NH_2 \cdot CO \cdot CH_2 \cdot CHBr \cdot COOH$, is readily obtained; it forms large crystals melting at 146° . and has the specific rotation $[\alpha]_D = -67.12^\circ$, -67.57° , and -44.3° in alcohol, ethylic acetate, and 20 per cent. sulphuric acid solutions respectively. When further treated with bromine and nitric oxide in acid or alkali solution, it yields *lævobromosuccinic acid*, which crystallises in striated prisms melting and decomposing at 173° , and has the specific rotations of $[\alpha]_D = -72.6^\circ$ to -72.7° and -67.92° in ethylic acetate and alcohol respectively; it is less soluble in the ordinary reagents than its known racemic isomeride. The *methylic* salt boils at 130° under 22 mm. pressure, and has the rotation $[\alpha]_D = -46^\circ$ in a 50-mm. tube; the *dextro*-isomeride boils at 126° under 18 mm., and has the rotation $[\alpha]_D = +48.3^\circ$ in a 50-mm. tube; the discrepancies are due to the readiness with which these compounds change into inactive methylic fumarate on distillation. The author has repeated and confirmed Piria's and Pasteur's statements respecting the conversion of asparagine and aspartic acid into *lævomalic acid*, and Tilden and Marshall's observation (*Trans.*, 1895, 494) that asparagine yields *lævochlorosuccinic acid* when treated with nitrosyl chloride.

Lævoasparagine can therefore be converted into *lævobromo*- or *chloro-succinic acid*, and also (*Abstr.*, 1893, i, 250) into the *dextro*-rotatory isomerides of these compounds; the somewhat remarkable result is thus obtained, that by treating an optically active substance containing only one asymmetric carbon atom with inactive reagents at relatively low temperatures, either optical isomeride of the substance formed may be obtained at will. W. J. P.

Thiosinamine (Allylthiocarbamide) and its Halogen Additive Products. By J. GADAMER (*Arch. Pharm.*, 1895, **233**, 646—684).—A substance, $C_4H_8N_2S, 2AgNO_3$, may be obtained by adding excess of a 10 per cent. solution of silver nitrate to a dilute aqueous or alcoholic solution of allylthiocarbamide, acidified with a drop of nitric acid, and is deposited, after a short time, in the form of grey, matted needles. It was obtained in an impure state by Falke (*Diss.*, 1893). When dissolved in water, it decomposes, and the solution subsequently deposits a new compound, $C_4H_8N_2S, AgNO_3$, which crystallises from water in long, silky needles. Picric acid displaces one molecular proportion of nitric acid from these compounds, the substances formed having the compositions $C_4H_7N_2S, Ag, C_6H_3N_3O_7, AgNO_3$, and



respectively; they are amorphous, but the former becomes crystalline spontaneously.

A compound, $C_4H_8N_2S, HgCl_2$, is obtained by the action of mercurous chloride on an aqueous solution of allylthiocarbamide, or by the action of allylthiocarbamide on the compound $C_4H_8N_2S, 2HgCl_2$. It crystallises in large prisms, which have the remarkable property of being half transparent, half opaque.

The interaction of allylthiocarbamide and mercuric cyanide yields the compounds $5C_4H_8N_2S, Hg(CN)_2$, forming large, shining crystals resembling those of mercuric cyanide, and $2C_4H_8N_2S, Hg(CN)_2$, which is obtained as grey, microcrystalline aggregates.

Cuprous chloride yields the compounds $C_4H_8N_2S, CuCl$, first obtained by Falke (*loc. cit.*), and $(C_4H_8N_2S)_3, Cu_2Cl_2$, which forms small, shining crystals.

When allylthiocarbamide is triturated with mercury, it yields mercuric sulphide and a new compound, which is a yellowish mass, soluble in alcohol, and melting at 79—80°. With allylthiocarbamide, copper and silver yield compounds of unknown constitution.

Methylallylthiocarbamide dibromide, $C_5H_{10}N_2SBr_2$, is formed on mixing alcoholic solutions of methylallylthiocarbamide and bromine. It forms large, white crystals, very soluble in water, and melts at 145—146°; the *picrate* melts at 181—182°. The *chlorobromide*, $C_5H_{10}N_2SBrCl$, obtained from the dibromide by the action of silver chloride, is readily soluble in water, and melts at 120—123°. The *platinochloride* is obtained as large, yellow, nodular aggregates; the *urochloride* is crystalline, melts at 80°, and dissolves sparingly in water.

Dimethylallylthiocarbamide is obtained on mixing alcoholic allylthiocarbamide and dimethylamine in molecular proportion; it is a liquid, crystallising only at the temperature produced by a mixture of solid carbonic anhydride and ether. The *dibromide*, which crystallises in large, white needles, melting at 207·5—208°, is very soluble in water, dissolving less readily in alcohol; the *chlorobromide* forms large, transparent, colourless crystals, and melts at 191—192°. The *urochloride* is deposited as a red oil, which gradually becomes crystalline; it melts at 70°. The *platinochloride* is more readily soluble, and crystallises in shining, yellow needles.

Allylthiocarbamide combines with trimethylamine at a temperature of 150–160°, forming an oily liquid. *Trimethylallylthiocarbamide dibromide* is an indistinctly crystalline mass, which is insoluble in alcohol, and yields a pale yellow *platinochloride*.

Dimethylallylthiocarbamide unites with silver nitrate, and with cuprous chloride. The *silver compound*, $C_6H_{12}N_2S, AgNO_3$, crystallises in needles, and yields a well crystallised *picrate*. The *copper compound*, $C_6H_{12}N_2S, CuCl$, was obtained in small, brownish crystals. Both compounds yield metallic sulphides when heated with aqueous ammonia. On mixing alcoholic solutions of dimethylallylthiocarbamide and mercuric chloride, a voluminous precipitate is produced.

When triturated with mercury in presence of alcohol, dimethylallylthiocarbamide is attacked, and a stable mercury compound is formed, together with mercuric sulphide.

The author regards it as highly probable that dimethylallylthiocarbamide has the constitution $NMe_2 \cdot C(SH) : N \cdot C_3H_5$. A. L.

Thio-Compounds of the Uric acid Group. By EMIL FISCHER and LORENZ ACH (*Annalen*, 1895, 288, 157–176).—*Thiouramil*, $CO < \begin{smallmatrix} NH \cdot C(SH) \\ NH - - CO \end{smallmatrix} > C \cdot NH_2$, is prepared in the following manner.

Potash is added to uric acid (60 grams), suspended in warm water (2,400 c.c.) until a clear solution is obtained; this is diluted with water (1,400 c.c.), treated with a freshly prepared solution of ammonium sulphide (1,000 c.c.), and heated for 5–6 hours at 155–160°. The clear liquid thus obtained, on cooling, deposits the ammonium derivative of thiouramil, and a further quantity of the product is obtained by removing ammonia and ammonium sulphide, and rapidly evaporating the solution, which is then acidified with glacial acetic acid. Thiouramil dissolves in 500–600 parts of boiling water, and separates in minute leaflets or prisms as the liquid cools; it is readily soluble in concentrated sulphuric acid, and is precipitated on diluting the liquid with water. Solutions in cold alkalis rapidly become red when exposed to the air. Cold concentrated nitric acid and the warm dilute acid act on thiouramil, giving rise to sulphuric acid and alloxan; thiouramil gives the murexide reaction, which can also be obtained by the use of chlorine water as the oxidising agent. A fir splinter is at once stained orange when immersed in a neutral or acid solution of thiouramil. Chlorides of the heavy metals yield a white precipitate with an aqueous solution of thiouramil; silver nitrate gives rise to a gelatinous precipitate, which becomes black when heated, or on treatment with ammonia. The *potassium* derivative crystallises in yellowish needles or prisms containing $1H_2O$, which is lost at 130°; the *sodium* derivative also forms yellow needles containing $1H_2O$, which is lost at 105°. The *ammonium* derivative crystallises in lustrous, golden-yellow leaflets, dissolving with difficulty in cold water and ammonium sulphide. When heated with hydrochloric acid for four hours at 150°, thiouramil is converted into a mixture of ammonium chloride and glycocine hydrochloride. *Methylthiouramil*, $C_5N_3H_7SO_2$, is obtained by agitating methylic iodide with a solution of the potassium derivative in water; it crystallises from hot water in stellar aggre-

gates of needles, and darkens at 230° when rapidly heated, melting and decomposing at $252-253^{\circ}$ (uncorr.). The neutral solution does not stain fir-wood, but colour is developed in the fibre on adding hydrochloric acid; it gives the murexide reaction when oxidised with chlorine water. The methyl derivative dissolves readily in hot mineral acids, and also in cold alkalis and alkali carbonates; on adding alcohol to the solution in caustic soda, the *sodium* derivative separates in minute, slender needles. Nitric acid oxidises the methyl derivative yielding alloxan, and when the substance is heated with hydrochloric acid for four hours at 150° , carbonic anhydride, ammonia, and methylic mercaptan are produced. *Ethenylthiouramil*, $C_6N_3H_5SO_2$, is obtained by heating the ammonium derivative in a reflux apparatus with acetic anhydride; it dissolves in 210–220 parts of boiling water, from which it separates in needles, melting, when rapidly heated, at $220-221^{\circ}$ (uncorr.). The substance dissolves in hot glacial acetic acid, concentrated mineral acids, and hot dilute alkalis, the *sodium* derivative being precipitated in slender needles on adding alcohol to the solution in caustic soda; silver nitrate forms a gelatinous precipitate when treated with the solution in ammonia, and this consists of the *silver* derivative, which crystallises from hot ammonia in minute, slender prisms. The ethenyl derivative gives the murexide reaction.

Azurilic acid, $C_4H_3N_3O_3$, is obtained by treating an alkaline solution of uric acid with a large excess of ammonium sulphide which has been kept for many months; a mixture of compounds is formed, and after treating this product with dilute nitric acid at $50-60^{\circ}$, azurilic acid is separated in the form of its *silver* derivative. If rapidly heated, the substance becomes coloured at 245° , and decomposes at 275° , when the odour of hydrogen cyanide becomes perceptible. It dissolves in 55 parts of hot water, from which it crystallises on cooling, and is also soluble in alcohol. It is readily soluble in alkalis and alkali carbonates, the solution in caustic soda yielding the *sodium* derivative on adding alcohol; it gives the murexide reaction.

β -Thiopseudouric acid, $CO < \begin{smallmatrix} NH \cdot C(SH) \\ NH - CO \end{smallmatrix} > C \cdot NH \cdot CO \cdot NH_2$, is obtained by boiling an aqueous solution of potassium cyanate with thiouramil; it crystallises in prisms, and contains $1H_2O$, which is lost at 130° . The acid is soluble in hot water, but dissolves with difficulty in boiling alcohol; alkalis and alkali carbonates dissolve it readily, and when silver nitrate is added to the solution in ammonia, a colourless, gelatinous precipitate is formed, becoming black when heated. Staining of fir-wood is only effected after prolonged boiling, but the murexide reaction is easily produced.

Oxalyldithiouramil, $C_2O_2(C_4H_4N_3SO_2)_2$, is obtained by adding the foregoing acid to fused oxalic acid, and heating the clear liquid until the oxalic acid is removed; it is a crystalline powder, dissolving in 400 parts of hot water, and is slowly converted into oxalic acid and thiouramil under the influence of hot, concentrated alkalis.

β -Methylthiopseudouric acid, $CO < \begin{smallmatrix} NH \cdot C(SMe) \\ NH - CO \end{smallmatrix} > C \cdot NH \cdot CO \cdot NH_2$, is

produced when the methyl derivative of thiouramil is heated on the water bath with an aqueous solution of potassium cyanate; it crystallises from hot water in colourless needles, and when rapidly heated darkens at 290° , and decomposes at 350° . The acid is soluble in 400 parts of hot water, but dissolves with great difficulty in alcohol; in alkalis, it is readily soluble, the metallic derivatives being decomposed by glacial acetic acid, and therefore differing from those of β -thiopseudouric acid, which are indifferent towards this agent. The acid gives the murexide reaction; the *silver* derivative is soluble in ammonia, and the *potassium* derivative crystallises in pale yellow needles, becoming darker on exposure to air.

Thiodimethyluramil, $\text{CO} < \begin{smallmatrix} \text{NMe} \cdot \text{C}(\text{SH}) \\ \text{NMe} - \text{CO} \end{smallmatrix} > \text{C} \cdot \text{NH}_2$, is obtained by heating dimethyluric acid, dissolved in ammonia, with freshly prepared ammonium sulphide for two hours at $135-140^{\circ}$; when rapidly heated, it begins to undergo change above 200° , and is completely decomposed about 300° . It dissolves in 70 parts of hot water, and crystallises in colourless needles, which become green in the air; it is readily soluble in hot alcohol, and crystallises in slender prisms. It dissolves readily in alkalis and alkali carbonates, and in other respects resembles thiouramil. M. O. F.

Hydrazides and Azides (Azoimides) of Carbonic acid. By THEODOR CURTIUS and KARL HEIDENREICH (*J. pr. Chem.*, 1895 [2], 52, 454—489; compare Abstr., 1894, i, 166).—Semicarbazide hydrochloride melts at 175° (Abstr., 1894, i, 165). Carbamic azoimide (carbaminazoimide, Abstr., 1895, i, 252) melts at 97° .

Carbohydrazide, previously called carbazide (Abstr., 1894, i, 166), melts at 152° ; its *hydrochloride*, $\text{CO}(\text{NH} \cdot \text{NH}_2)_2 \cdot 2\text{HCl}$, melts at 210° , and its *sulphate* melts and decomposes at 218° . A *diacetyl derivative* was prepared.

Carbazoimide has already been described as carbonyl nitride (Abstr., 1895, i, 12); attention is called to the analogy of its reactions to those of carbonyl chloride. The *silver derivative* of methenylcarbohydrazide, $\text{C}_2\text{H}_3\text{N}_4\text{OAg}$, is a white powder, stable in light.

Methylic azoimidocarbonate, $\text{N}_3 \cdot \text{CO}_2 \cdot \text{Me}$, is prepared by treating ammonium azoimide with methylic chlorocarbonate in ethereal solution. It is a colourless liquid, and boils at 102° , but is liable to explode at this temperature.

The hydrazine salt of dicarbamide (*loc. cit.*) melts at 197° ; the *silver salt*, $\text{C}_2\text{H}_3\text{N}_4\text{O}_2\text{Ag}$, is a white powder stable in light.

Hydrazine thiocyanate, $\text{N}_2\text{H}_4\text{SCN}$, is prepared by decomposing hydrazine sulphate with barium thiocyanate; it crystallises in tablets, melts at 80° , and dissolves freely in water and alcohol. When heated in a sealed tube at 100° for 4—5 hours, it yields *hydrazidothiocarbonamide*, $\text{NH}_2 \cdot \text{CS} \cdot \text{NH} \cdot \text{NH} \cdot \text{CS} \cdot \text{NH}_2$, which crystallises from hot water in long, colourless prisms, and melts at $214-215^{\circ}$; one part dissolves in 418.5 parts of water at 23° .

The remainder of the compounds described in this paper have already received notice in the places quoted. A. G. B.

A Derivative of Furfuraldehyde from Lævulose. By JOSEPH KIERMAYER (*Chem. Zeit.*, 1895, **19**, 1003—1005; compare Düll, this vol., i, 121).—The product obtained by Düll, by the action of oxalic acid on lævulose is shown by the author to be a derivative of furfuraldehyde. It is most readily prepared from cane sugar, as the glucose produced by inversion is not acted on. A 30 per cent. aqueous solution of cane sugar is heated with 0.3 per cent. oxalic acid for 3 hours under a pressure of three atmospheres; the mixture is neutralised with calcium carbonate, treated with basic lead acetate, and then extracted with ether or ethylic acetate. The aldehyde forms a colourless syrup, which rapidly turns yellow on exposure to the air. It is readily soluble in water, alcohol, and ethylic acetate, more sparingly in ether. It begins to boil and froth at 60°, but even when the temperature has reached 200° only a slight distillate is obtained, and this consists of furfuraldehyde; on further heating, however, it is completely decomposed, and cannot be distilled even under diminished pressure. Its alcoholic solution gives a deep scarlet coloration with thymol and sulphuric acid, and a deep red with phloroglucinol. Both are extremely delicate reactions. It acts as a strong reducing agent towards ammoniacal silver nitrate and Fehling's solution. The author considers it is probably β -hydroxy- δ -methylfurfuraldehyde, $\text{OH}\cdot\text{C}_4\text{OHMe}\cdot\text{COH}$. The phenylhydrazone forms golden-yellow crystals and melts at 138°, the anti-aldoxime melts at 77—78°, and if allowed to remain for some time in alkaline solution is converted into the syn-aldoxime, which melts at 108°. The syn-aldoxime is converted back again into the anti-compound when heated for 30 mins. at 115—120°. The author shows that a similar treatment converts furfur-syn-aldoxime into furfur-anti-aldoxime.

When the aldehyde is oxidised by ammoniacal silver nitrate, it yields β -hydroxy- δ -methylpyromucic acid, $\text{OH}\cdot\text{C}_4\text{OHMe}\cdot\text{COOH}$; this is readily soluble in water, sparingly in ether, melts at 148°, and at the same time undergoes decomposition. Its solution is coloured yellow by ferric chloride. The silver salt crystallises with $1\text{H}_2\text{O}$ in colourless prisms, it is sparingly soluble in water, and readily blackens on exposure to light. The copper and calcium salts are also described. The benzoyl derivative, $\text{C}_6\text{H}_5\text{O}_2\cdot\text{COPh}$, crystallises in long needles, melts at 55° and is readily soluble in ethylic acetate, benzene, and alcohol.

When the aldehyde is heated with oxalic acid and water under a pressure of three atmospheres, it is converted into levulinic acid. Reasons for considering the aldehyde as a β -hydroxy-compound are given.

When the pure aldehyde is allowed to remain over sulphuric acid, in the course of a few days it loses water and forms methylfurfuraldehyde oxide, $\text{O}(\text{C}_4\text{OHMe}\cdot\text{COH})_2$; this oxide is also obtained by the distillation of the aldehyde. It crystallises in long feathery needles, melts at 112°, is sparingly soluble in hot water and in ether, and insoluble in benzene and acetic acid. The aqueous solution readily reduces ammoniacal silver nitrate and Fehling's solution, and gives colorations with phenols. The anilide, $(\text{C}_6\text{H}_5\text{O}\cdot\text{NPh})_2\text{O}$, forms colourless plates and melts at 124°, the phenylhydrazone,

$(C_6H_5O:N:NHPh)_2O$, melts at 139° , and the *syn*-aldoxime at 167 – 168° . This oxime is soluble in ethylic acetate and acetone, only sparingly in chloroform, ether, and benzene, and more readily in hot dilute alcohol than in concentrated.

Sorbinose, when heated with aqueous oxalic acid, also yields the same methylhydroxyfurfuraldehyde. Dextrose, on the other hand, is not acted on by a 0.5 per cent. solution of oxalic acid, lactose behaves similarly.

J. J. S.

Synthesis of β -Methylpentamethylenecarboxylic acids. By WILHELM EULER (*Ber.*, 1895, 2952–2959).—Pyrotartaric nitrile, $CN \cdot CHMe \cdot CH_2 \cdot CN$ (Claus, *Annalen*, **191**, 33), is obtained by heating allylic iodide with potassium cyanide in alcoholic solution and fractionating the product; it boils at 240 – 260° , or at 130 – 140° under 20 mm. pressure, but the yield of it is only 5 per cent. of the weight of the allylic iodide, the chief product of the reaction being β -ethoxybutyronitrile. By reducing it with sodium in alcoholic solution it is converted into the diamine (Oldach, *Abstr.*, 1887, 735), the *dihydrochloride* of which melts at 144 – 145° . When this salt is decomposed, in ice-cold solution, with the equivalent quantity of silver nitrite, and the filtered solution slowly distilled until the temperature reaches 140° , β -methyltetramethylene glycol, $OH \cdot CH_2 \cdot CHMe \cdot CH_2 \cdot CH_2 \cdot OH$ is obtained, together with an oil boiling between 70° and 130° ; the latter is probably a mixture of the unsaturated alcohols, $OH \cdot CH_2 \cdot CHMe \cdot CH \cdot CH_2$ and $CH_2 \cdot CMe \cdot CH_2 \cdot CH_2 \cdot OH$, as it forms a *dibromo-additive compound*, and also a *monacetate* boiling at 120 – 130° ; a hydrocarbon, $CH_2 \cdot CMe \cdot CH \cdot CH_2$, is probably formed in addition. The glycol boils at 115 – 130° under 20 mm. pressure; when it is saturated with hydrogen bromide at 0° and then heated at 110° , it yields β -methyltetramethylene *dibromide*. If this is heated with ethylic disodiummalonate in alcoholic solution, and the fraction of the product that boils above 135° under 18 mm. pressure is hydrolysed with 10 per cent. aqueous alcoholic potash, β -methylpentamethylenedicarboxylic acid, $\begin{array}{c} CH_2-CH_2 \\ | \\ CHMe-CH_2 \end{array} > C(COOH)_2$, is obtained.

This melts at 140 – 142° , and then loses carbonic anhydride, the *monocarboxylic acid* finally distilling over at about 220° . Of the latter only a few drops were obtained, although 8 kilos. of allylic iodide were worked up; its *calcium salt*, with $5H_2O$, and the *silver salt* were, however, prepared and analysed.

C. F. B.

New treatment of the Benzene Problem: Derivatives of Thymotic acid. By GEORG HEYL and VICTOR MEYER (*Ber.*, 1895, **28**, 2776–2798).—In order to obtain some insight into the constitution of the benzoic acids, and, therefore, of the aromatic compounds, the etherification of certain fatty acids has been studied on the same lines as that of the substituted benzoic acids. Acids such as aconitic acid,



and tricarballic acid, $\text{COOH}\cdot\text{CH}_2\cdot\text{CH}(\text{COOH})\cdot\text{CH}_2\cdot\text{COOH}$, readily yield tri-etheral salts when treated with alcohol and hydrogen chloride at 0° , whilst the corresponding aromatic acid, hemimellitic acid, does not yield a tri-salt under these circumstances. This shows that the reaction characteristic of aromatic acids does not hold with others containing the same groups, since the three carboxyl groups of their acids are adjacent.

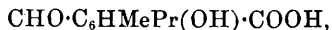
The aromatic acids may be supposed to contain either the group $\text{COOH}\cdot\text{C}\begin{smallmatrix} \diagup \text{C} \\ \diagdown \text{C} \end{smallmatrix}$ or $\text{COOH}\cdot\text{C}\begin{smallmatrix} \text{C} \\ \diagdown \text{C} \\ \diagup \text{C} \end{smallmatrix}$, according to the benzene formula

which is accepted. The authors, therefore, next studied the etherification of certain fatty acids which also contain these groups. Triphenylacrylic acid, $\text{COOH}\cdot\text{C}\begin{smallmatrix} \text{CPh}_2 \\ \diagdown \text{Ph} \end{smallmatrix}$, contains the first whilst the second is present in triphenylacetic acid, $\text{COOH}\cdot\text{CPh}_3$. The essential point is, that the group $\text{COOH}\cdot\text{C}$ is connected with *tertiary* carbon atoms; the phenyl group is chosen simply because the carbon atom which is directly combined with the group $\text{COOH}\cdot\text{C}$ is a tertiary one. Neither of these acids is completely etherified by alcoholic hydrogen chloride in the cold, triphenylacrylic acid yielding 22.3 per cent., and triphenylacetic acid only 3.45 per cent. of ethereal salt. When treated with hydrogen chloride in boiling alcoholic solution, the triphenylacrylic acid gives 97 per cent. of ethereal salt, whilst triphenylacetic acid only gives 22.3 per cent.; the behaviour of triphenylacetic acid is therefore precisely analogous to that of a diorthosubstituted benzoic acid. It follows that substances which

contain the group $\text{COOH}\cdot\text{C}\begin{smallmatrix} \text{C} \\ \diagdown \text{C} \\ \diagup \text{C} \end{smallmatrix}$ behave, in this respect, as aromatic substances, whilst those which contain the group $\text{COOH}\cdot\text{C}\begin{smallmatrix} \diagup \text{C} \\ \diagdown \text{C} \end{smallmatrix}$ do not.

Triphenylacrylic acid may be prepared from benzophenone chloride and benzylic cyanide, as already described (Abstr., 1895, i, 542), or by heating benzophenone chloride with methylic phenylacetate. In this case, it is accompanied by a small amount of *diphenylindone*, which forms dark orange-red crystals, and melts at $150-151^\circ$. Triphenylpropionic acid is readily etherified by boiling alcoholic hydrogen chloride, so that the characteristic behaviour of triphenylacetic acid is not merely due to the presence of three phenyl groups.

The authors have also endeavoured to resolve nitrothymotic acid, $\text{NO}_2\cdot\text{C}_6\text{HMePr}(\text{OH})\cdot\text{COOH}$, and formylthymotic acid,



which contain six different groups, into optically active constituents, but without success. Similar experiments with *meta*-hydroxybenzoic acid also gave a negative result.

Nitrothymotic acid is obtained by the direct nitration of thymotic acid, and crystallises in yellowish plates, melting at $173-175^\circ$.

Formylthymotic acid is prepared by heating thymotic acid with chloroform and aqueous soda. It melts at 180—185°. A. H.

The Benzene Problem. By JULIUS W. BRÜHL (*Ber.*, 1895, **28**, 2981—2986).—The author thinks that no definite conclusions respecting the structure of the benzene ring can be drawn from the work of Heyl and V. Meyer (preceding abstract). By means of figures, it is shown, that from stereochemical considerations triphenylacetic acid would probably be difficult to etherify. J. J. S.

Action of Nascent Bromine on Benzene Derivatives. By WILHELM VAUBEL (*J. pr. Chem.*, 1895, [2], **52**, 417—423; compare Abstr., 1894, i, 94, 453).—Amido- and hydroxy-derivatives, be they primary, alkylised or acetylated, when united directly to the nucleus, possess, beyond all other substituents, the property of facilitating the entrance of bromine in place of nucleal hydrogen. The bromine always takes the ortho- and para-positions with regard to the NH_2 - and OH-groups. None of the usual substituents—such as CH_3 , NO_2 , halogen, SO_3H , COOH , N:NR , N:NCI —prevents the entrance of bromine, should the substituent itself occupy the ortho- or para-position to NH_2 or OH. Exceptions are NH_2 and OH themselves; these in the ortho- or para-position to each other hinder bromination, and the action of bromine effects oxidation.

The carboxyl and sulphonic groups are displaced by bromine when they are in the ortho- or para-position to an amido- or hydroxy-group. This tendency remains when another substituent (for example, CH_3 or NO_2), is in the meta-position with respect to the said groups. An SO_3H or COOH group in the meta-position relatively to NH_2 or OH is not displaced by bromine.

Alkylised or acetylated OH and NH_2 groups exert a smaller orienting influence on bromine. The dialkylised amido-group shows this to a greater extent than the monalkylised group. A. G. B.

Note (Synthesis of Aromatic Hydrocarbons). By PAUL JANNASCH (*Ber.*, 1895, **28**, 2823).—In order to avoid clashing with Töhl (this vol., i, 16), the author points out the direction in which he is pursuing his researches on the substituted benzenes. A. H.

Symmetrical Trinitrobenzene. By CORNELIUS A. LOBRY DE BRUYN and FREDERIK H. VAN LEENT (*Rec. Trav. Chim.*, 1895, **14**, 150—155; compare Abstr., 1895, i, 574).—When the calculated quantity (1 mol.) of a very concentrated solution of potassium hydroxide is added to a solution of symmetrical trinitrobenzene in 96 per cent. methylic alcohol, red crystals of a substance are deposited after a time, whilst dinitroanisole remains dissolved in the mother liquor. The new substance has the composition represented by the formula $[\text{C}_6\text{H}_3(\text{NO}_2)_3, \text{MeOK}]_2 + \text{H}_2\text{O}$. If heated on platinum foil, it detonates violently, and, when treated with dilute acids, symmetrical trinitrobenzene is regenerated. When sodium hydroxide was used instead of potassium hydroxide, no analogous crystalline

derivative could be isolated, although the solution became red. If ethylic alcohol is substituted for methylic alcohol, the reducing action of the former is so great that brown, amorphous compounds are alone produced.

A. R. L.

Phenylnitromethane (exo-Nitrotoluene). By ARNOLD F. HOLLEMAN (*Rec. Trav. Chim.*, 1895, **14**, 121—130).—The observations on the boiling point of phenylnitromethane (phenylnitromethane, *Abstr.*, 1895, **i**, 455) have been confirmed by Gabriel in a communication to the author, who has prepared phenylnitromethane by the method previously described by himself (*loc. cit.*), and also by Gabriel's method (*Abstr.*, 1884, 902). The products had the same boiling point in both cases, and gave a benzenazo-derivative melting at 101°.

The action of one equivalent of bromine on exo-nitrotoluene furnishes a mixed product. Exo-nitrotoluene dissolves in concentrated sulphuric acid, but the product soon resinifies.

Exometadinitrotoluene, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{NO}_2$, is obtained when phenylnitromethane is dropped into cooled nitric acid of sp. gr. 1.5 (7 parts), care being taken that the temperature does not exceed 10° during the reaction. The new compound is colourless, melts at 94°, and is soluble in the usual solvents, but crystallises best from glacial acetic acid. Its constitution is proved by the fact that it yields metanitrobenzoic acid on treatment with alkaline permanganate. The *sodium* and *potassium* derivatives are red, and crystallise in needles; their solutions are faintly alkaline towards litmus, and are decolorised on addition of an acid, yielding the parent compound. Inasmuch, however, as exometadinitrotoluene is a strong acid it cannot be used as an indicator. The solutions of the alkali salts give, with silver nitrate, a gelatinous precipitate, which blackens on being heated; with copper sulphate (heated), blue triclinic crystals; with lead acetate, a yellowish-white precipitate, and with mercuric chloride a white, amorphous precipitate.

An *additive compound*, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{NO}_2 \cdot \text{NH}_3 \cdot \text{H}_2\text{O}$, separates in yellow, silky needles, when an alcoholic solution of exometadinitrotoluene is treated with alcoholic ammonia, ether being subsequently added. It dissociates very readily, becoming white on exposure to the air for a single day.

From the mother liquor obtained in the preparation of exometadinitrotoluene, an isomeric substance was isolated, which also was found to yield metanitrobenzoic acid on oxidation; the specimen analysed melted between 65° and 80°. The colour of the alkali salts of this substance is yellow, and is only slowly discharged when a solution is treated with an equivalent of acid, exometadinitrotoluene then separating. The phenomenon can be explained by assuming that the yellow anions are transformed into colourless tautomeric anions. Determinations of the molecular conductivity of the solution during its change of colour, which diminishes in proportion as the colour vanishes, lead to the same conclusion.

It seems probable, therefore, that exometadinitrotoluene exists in two modifications, one of which—that forming yellow salts—contains the group NOH.

A. R. L.

Ozotoluene. By ADOLPHE RENARD (*Compt. rend.*, 1895, **121**, 651—652).—The action of ozone on commercial toluene yields a black, tarry, acid, non-explosive product, but if after the action of the ozone has continued from 10 to 12 hours, the toluene is separated, washed with alkali, redistilled, and again heated with ozone at 0° , it yields *ozotoluene*, $C_7H_5O_6$, a white, translucent, gelatinous substance, which becomes white and opaque if the toluene is evaporated in a current of air. In dry air, it begins to decompose at 8° or 10° , and in moist air it is decomposed at once. It detonates when heated or struck, but less readily than ozobenzene (*Abstr.*, 1895, i, 593). In contact with concentrated aqueous potash, it decrepitates briskly, but, unlike ozobenzene, it does not explode in contact with ammonia or concentrated sulphuric acid. Water decomposes it with development of heat and formation of formic and benzoic acids, a result which shows that the benzene nucleus remains intact.

Pure orthoxylene, when treated with ozone at 0° , likewise yields a white explosive compound, similar to ozobenzene and ozotoluene.

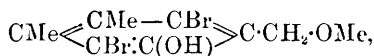
C. H. B.

Conversion of Nitriles into Amides by Hydrogen Peroxide.

By J. DEINERT (*J. pr. Chem.*, 1895, [2], **52**, 431—432).—The author has applied Radziszewski's method (*Abstr.*, 1885, 496) to sundry nitriles, and has obtained fair yields of the corresponding amides from benzonitrile, benzylic cyanide (in alkaline solution), paratoluenitrile, and β -naphthonitrile. Propionitrile and α -naphthonitrile gave very poor yields, whilst orthotoluenitrile was not converted at all.

A. G. B.

An Abnormal Tribromo-derivative of Pseudocumenol. By KARL AUWERS (*Ber.*, 1895, **28**, 2888—2902; compare the two following abstracts).—The remarkable reactions of the tribromo-derivative of pseudocumenol, which are described in the two following abstracts, seem to be best explained by the formula $CMe \begin{smallmatrix} CMe \\ CBr:C(OBr) \end{smallmatrix} CBr \begin{smallmatrix} CBr \\ C(OBr) \end{smallmatrix} CMe$. The methoxy-compound would then receive the formula



the methoxy-group having, by molecular change, been substituted for an atom of hydrogen of the methyl group, whilst this atom of hydrogen goes to form the hydroxyl group, which these derivatives undoubtedly contain. The formulæ of the remaining derivatives are given along with their special description.

A. H.

An Abnormal Tribromo-derivative of Pseudocumenol.

By KARL AUWERS and J. MARWEDEL (*Ber.*, 1895, **28**, 2902—2910; compare foregoing abstract).—Pseudocumenol yields two bromo-derivatives which contain the bromine atoms in the nucleus (Reuter, *Ber.*, **11**, 29). In addition to these, a third compound can be obtained by treating the phenol with bromine and acetic acid. This substance, *dibromopseudocumenol bromide*, $C_6Me_3Br_2 \cdot OBr$, crystallises in large, flat needles, and melts at $125-126^{\circ}$. It does not dissolve immediately in

alkalis, but is decomposed by them after a time. The bromine atom very readily enters into reaction, and the substance produced is decomposed by alcohols if left in contact with them; by silver nitrate, with formation of silver bromide; and by potassium iodide, iodine being liberated. *Dibromomethoxy-pseudocumenol*, $\text{OH}\cdot\text{C}_6\text{Me}_2\text{Br}_2\cdot\text{CH}_2\cdot\text{OMe}$, is obtained by boiling the tribromo-derivative with methylic alcohol. It crystallises in matted, silky needles, melts at $91-92^\circ$, and is readily soluble in alkalis, forming solutions from which it is reprecipitated by acids, even after boiling. This substance contains a hydroxyl group, and yields a *benzoate* which crystallises in fascicular groups of silky needles melting at 120° . *Ethoxydibromopseudocumenol* closely resembles the methoxy-compound, and crystallises in silky needles melting at $85-87^\circ$. The *benzoate* also forms needles, and melts at $109-110^\circ$. The tribromo-derivative also reacts with aniline to form a *compound* of the formula $\text{OH}\cdot\text{C}_6\text{Me}_2\text{Br}_2\cdot\text{CH}_2\cdot\text{NHPh}$, which crystallises in rhomboid forms, and melts at $134-134.5^\circ$. This substance forms salts, both with alkalis and acids; the *sodium salt* crystallises in silky needles, which are very readily soluble in water, and are decomposed by carbonic anhydride. The salts with acids are crystalline, and almost insoluble in cold water, scarcely soluble in hot water; the *bromide* melts at about 200° , the *chloride* at about 205° , the *nitrate* with decomposition at about 172° , and the *sulphate* indefinitely from $135-150^\circ$; the *acetate*, which crystallises in prisms having an adamantine lustre, melts at $223-225^\circ$. The *piperidine compound* from the tribromo-derivative forms concentric groups of slender, white needles melting at 91° ; it resembles the aniline derivative, but its salts with acids are somewhat more readily soluble in water. The *bromide* melts at $207-208^\circ$; the *benzoate* crystallises in small needles melting at $136.5-137.5^\circ$. When it is heated on the water bath, piperidine is given off, whilst *tetrabromodihydroxytetramethylstilbene*, $\text{C}_2\text{H}_2(\text{C}_6\text{Me}_2\text{Br}_2\cdot\text{OH})_2$, remains; this crystallises in matted needles, melts at $232.5-234^\circ$, is readily soluble in alkalis without decomposition, but only very sparingly in the ordinary solvents. The *ethyl ether* forms lustrous plates, and melts at $171-172.5^\circ$; its molecular weight, determined by the cryoscopic method, agrees with the formula $\text{C}_{22}\text{H}_{24}\text{Br}_4\text{O}_2$. A. H.

An Abnormal Tribromo-derivative of Pseudocumenol. By KARL AUWERS and S. AVERY (*Ber.*, 1895, 28, 2910-2923; compare the foregoing abstracts).—When the tribromo-derivative of pseudocumenol is brought into contact with dimethylaniline, the *bromide* of the dimethylaniline derivative separates in the form of leaf-like crystals melting at $234-236^\circ$. The free base, $\text{OH}\cdot\text{C}_6\text{Me}_2\text{Br}_2\cdot\text{CH}_2\cdot\text{NMe}_2\text{Ph}$, crystallises in transparent needles melting at 124° , and resembles the aniline compound in its general properties. The *hydrochloride* crystallises in nacreous plates melting at $216-220^\circ$; the *nitrate* melts at 200° , and the *sulphate* at $86-90^\circ$; all these salts are insoluble in water, and are decomposed by boiling water. The *benzoate* melts at $156-158^\circ$. The presence of the hydroxyl group in this compound is further shown by the fact that it unites with phenylcarbimide to form a *phenylurethane derivative*,



which melts at 186—189°.

When the tribromo-derivative is treated with pyridine, the *hydrobromide* of a *pyridine derivative*, $\text{OH}\cdot\text{C}_6\text{Me}_2\text{Br}_2\cdot\text{CH}_2\cdot\text{C}_5\text{NH}_5\text{Br}$, is formed; this is insoluble in water, melts at 234—236°, and crystallises with $1\text{H}_2\text{O}$ from an acetic acid solution of hydrogen bromide. When it is treated with alkalis, the corresponding base is not liberated, but a *yellow substance*, which is very unstable, is produced; this has the formula $\text{C}_9\text{H}_8\text{Br}_2\text{O}\cdot\text{C}_5\text{NH}_5 + 2\text{H}_2\text{O}$, and, when heated with aqueous alkalis, yields tetrabromodihydroxytetramethylstilbene, identical with that obtained by heating the piperidine derivative on the water bath (compare the foregoing abstract). When the yellow compound, however, is heated alone on the water bath or boiled with water, it yields *dibromohydroxypseudocumenol*, $\text{OH}\cdot\text{C}_6\text{Me}_2\text{Br}_2\cdot\text{CH}_2\cdot\text{OH}$. The same substance can be more conveniently prepared by boiling the tribromo-derivative itself with aqueous acetic acid or aqueous acetone. It crystallises from benzene in lustrous white needles, and melts at 166°; it unites with some difficulty with phenylcarbimide, forming a *compound*, $\text{C}_9\text{H}_8\text{Br}_2\text{O}\cdot\text{O}\cdot\text{CO}\cdot\text{NPh}$, which is a white, crystalline powder melting at 135°. Potassium ferricyanide oxidises the hydroxy-derivative, forming an insoluble substance which has the formula $(\text{C}_9\text{H}_8\text{Br}_2\text{O})_x$, and melts at 200—205°; the constitution of this product has not yet been ascertained. The *ether of dibromohydroxypseudocumenol*, $(\text{OH}\cdot\text{C}_6\text{Me}_2\text{Br}_2\cdot\text{CH}_2)_2\text{O}$, is formed when the hydroxy-compound is boiled with acetic acid and, indirectly, when the tribromo-derivative is dissolved in acetic acid, water added to the hot solution, and the whole boiled. It crystallises in slender, silky needles, and melts at 252°; it is readily soluble without decomposition in aqueous alkalis, and yields a *diacetate*, which melts at 216°. The *acetate of dibromohydroxypseudocumenol* is formed along with the ether when the tribromo-derivative is heated with aqueous acetic acid, and may also be prepared by boiling the same substance with glacial acetic acid and sodium acetate, and by treating the hydroxy-compound with acetic anhydride. It is insoluble in water, readily soluble in other solvents, and melts indefinitely at about 113°. When boiled with aqueous acetone, it yields dibromohydroxypseudocumenol. When it is shaken, or ground up with dilute aqueous soda, on the other hand, it yields tetrabromodihydroxytetramethylstilbene (compare foregoing abstract). The tribromo-derivative is reduced by zinc and glacial acetic acid, with formation of dibromopseudocumenol and the acetate of hydroxydibromopseudocumenol, accompanied by a small amount of a substance melting at 270—272°, the constitution of which has not been ascertained. A. H.

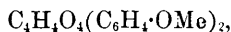
Derivatives of Benzoylcarbinol and of Diphenacyl. By VICTOR FRITZ (*Ber.*, 1895, **28**, 3028—3034; compare Hunaeus and Zincke, *Abstr.*, 1878, 223; E. Fischer, *Ber.*, **20**, 822; **26**, 2400; *Abstr.*, 1895, i, 440).—Benzoylmethylic phenylic ether, $\text{CH}_2\text{Bz}\cdot\text{OPh}$ (Möhlau, *Abstr.*, 1883, 332), does not reduce Fehling's solution, and is not decomposed at 100° by aqueous alcohol containing 5 per cent.

of hydrogen chloride. The *oxime* crystallises in small, colourless prisms, melts at 113—114° (uncorr.), and is readily soluble in alcohol, ether, benzene, and alkalis. The *phenylhydrazone* is readily soluble in ether and benzene, more sparingly in cold alcohol; it melts at 85—87°, and readily turns brown on exposure to the air.

Benzoylmethylic β-naphthyllic ether, $\text{CH}_2\text{Bz}\cdot\text{O}\cdot\text{C}_{10}\text{H}_7$, obtained by the action of bromacetophenone on the sodium derivative of β-naphthol, crystallises in small, colourless needles, and melts at 104—106° (uncorr.). Towards Fehling's solution and hydrochloric acid, it behaves in exactly the same way as the phenylic ether. The *oxime* melts at 144—145°. *Bisethylbenzoylcarbinol* was prepared by the ethylation of benzoyl carbinol (Fischer, Abstr., 1895, i, 440); it crystallises in colourless prisms, melts at 190—192°, and is readily soluble in hot alcohol or ether.

Bromodiphenacyl, $\text{COPh}\cdot\text{CHBr}\cdot\text{CH}_2\cdot\text{COPh}$, is obtained by the action of sodium and alcohol on an ice-cold solution of bromacetophenone in alcohol; it crystallises in small, colourless, glistening needles, melts at 161—162°, and is only sparingly soluble in alcohol and ether. When treated with alcohol and zinc dust, it yields diphenacyl (Kapf and Paal, Abstr., 1889, 147; Nötling and Kohn, Abstr., 1886, 349; Claus and Werner, Abstr., 1887, 827), and with alcohol and sodium amalgam yields a compound $\text{C}_{16}\text{H}_{18}\text{O}_2$. This crystallises in colourless needles, melts at 93—94°, is readily soluble in alcohol, ether, and benzene, and sublimes when heated above its melting point. It may also be obtained by the reduction of diphenacyl itself with sodium amalgam, and is probably *diphenyltetramethyleneglycol*, $\text{C}_2\text{H}_4(\text{CHPh}\cdot\text{OH})_2$. J. J. S.

New Salts of Guaiacol. By H. DUBOIS (*Chem. Centr.*, 1895, i, 209; from *Apoth. Zeit.*, 9, 952).—*Guaiacol succinate*,



crystallises in fine, silky needles, melts at 136°, is insoluble in water, sparingly soluble in alcohol or ether, but readily in chloroform, acetone, or hot light petroleum. Bromine readily forms substitution products. It is best prepared by dissolving guaiacol in slight excess of sodium hydroxide solution, cooling to 0°, and then adding the requisite quantity of succinic chloride while keeping well stirred. *Guaiacol phosphate*, $\text{PO}(\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{OMe})_3$, crystallises in hard, colourless plates, melts at 98°, is readily soluble in chloroform and acetone, but insoluble in water, ether, and light petroleum. It is readily hydrolysed by aqueous potash at 150°, and may be distilled under diminished pressure without decomposing. J. J. S.

Triresorcinol. By OSWALD HESSE (*Annalen*, 1895, 289, 61—70).—The *hydrochloride* of triresorcinol, $\text{C}_{18}\text{H}_{14}\text{O}_4\cdot\text{HCl}$, is obtained by heating resorcinol (4 grams) with glacial acetic acid (4—6 c.c.) and fuming hydrochloric acid (4 c.c.) in sealed tubes at 85° for 72 hours; it contains $1\text{H}_2\text{O}$, which is removed at 120°, and crystallises in small prisms which have a fire-red reflex and appear yellow by transmitted light. It is almost insoluble in organic solvents, but dissolves readily in

alkalis and alkali carbonates, forming yellowish-red solutions which, on dilution, exhibit intense, green fluorescence. *Triresorcinol*, $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{OH}$, obtained by prolonged treatment of the hydrochloride with boiling water, crystallises in short prisms which contain $2\frac{1}{2}\text{H}_2\text{O}$, and have a dark, bluish-red reflex, appearing yellow by transmitted light; it becomes anhydrous at 120° , and decomposes above 130° without previously melting. Although the substance dissolves sparingly in common solvents, the solutions exhibit intense green fluorescence; it dissolves in alkalis and alkali carbonates, cotton, wool, and silk being dyed yellow by these solutions. The *hydrobromide*, $(\text{C}_{18}\text{H}_{14}\text{O}_4)_4\cdot 5\text{HBr}$, is obtained by treating the solution in glacial acetic acid with concentrated hydrobromic acid; it is anhydrous, and, although scarcely soluble in cold water, it imparts an intense green fluorescence to this medium. The *diacetyl* derivative crystallises in brownish-red leaflets which melt and decompose at $260-270^\circ$.

Bromotriresorcinol hydrobromide, $\text{C}_{18}\text{H}_{13}\text{BrO}_4\cdot\text{HBr}$, is obtained by adding bromine to a solution of triresorcinol in hot acetic acid and immediately removing the crystals which separate; it contains $1\text{H}_2\text{O}$, and is decomposed by boiling water, yielding *bromotriresorcinol*, which dissolves readily in boiling water, and exhibits an intense green fluorescence in solution. If excess of bromine is employed, the substance is redissolved, and a *compound* is formed having the composition $(\text{C}_{18}\text{H}_{10}\text{Br}_4\text{O}_4)_2\cdot 5\text{HBr}$; this is readily soluble in boiling water, yielding an intense bluish-violet solution, whilst alkalis and ammonia develop a purple-violet coloration. *Tetrabromotriresorcinol*, $\text{C}_{18}\text{H}_{10}\text{Br}_4\text{O}_4$, is obtained by dissolving the foregoing compound in aqueous sodium hydrogen carbonate and treating the liquid with nitric acid; it is insoluble in cold water, and only sparingly soluble in the boiling liquid, yielding a bluish-violet solution. After removing the two products already mentioned, as obtained on brominating triresorcinol, the liquid contains *heptabromotriresorcinol*, $\text{C}_{18}\text{H}_7\text{Br}_7\text{O}_4$, a carmine-red compound having a bluish reflex; it contains $2\frac{1}{2}\text{H}_2\text{O}$, and is insoluble in water, dissolving readily, however, in organic solvents. Alkalis, alkali carbonates, and ammonia give rise to bluish-violet solutions which dye wool, cotton, and silk the same shade.

Barth and Weidel (Abstr., 1878, 61) have obtained diresorcinol and tetraresorcinol by the action of concentrated hydrochloric acid on resorcinol, and the formation of resacetophenone and resacetein or acetofluorescein under the influence of glacial acetic acid, has been also recorded.

M. O. F.

Action of Potassium Hydroxide and Ethoxide on Quinone.

By CHARLES ASTRE (*Compt. rend.*, 1895, **121**, 530—532).—When potassium ethoxide is added to a dilute solution of quinone in ether, a green compound, $\text{C}_6\text{H}_3\text{KO}_2 + \text{EtOH}$, is precipitated. It is stable in dry air or dry oxygen, but rapidly alters in moist air.

The action of concentrated alcoholic potash on quinone develops a large quantity of heat. With a very dilute alcoholic solution of quinone, a mixture of a blue and a yellowish-brown compound is obtained. The careful addition of alcoholic potash to a very dilute

etheral solution of quinone in an atmosphere of hydrogen yields a crystalline blue precipitate of the composition $C_6H_3KO_2 + H_2O$. It alters rapidly in presence of moist air or oxygen, or in contact with water or alcohol.

Attempts to obtain a dipotassium derivative of quinone were not completely successful, and the compound seems to be very unstable. A product with a composition corresponding with a compound of one molecule of dipotassium quinone with two molecules of alcohol is obtained on adding a large quantity of ether to a mixture of an alcoholic solution of quinone with excess of alcoholic potash.

C. H. B.

Peroxidised Potassium Derivatives of Quinone. By CHARLES ASTRE (*Compt. rend.*, 1895, **121**, 559—561; compare this vol., i, 18).—*Peroxidised dipotassium quinone*, $C_6K_2O_6$, a blackish, crystalline, very hygroscopic compound, is obtained by mixing alcoholic solutions of quinone and potassium hydroxide, heating the mixture at $70-75^\circ$, and passing a current of dry oxygen through it for eight to ten hours; it is very soluble in, and is decomposed by, water. The same product is obtained even in presence of a large excess of the alkali. *Peroxidised potassium quinone*, C_6KHO_6 , is a black compound obtained by dissolving the preceding compound in water and adding sufficient alcohol to bring the alcoholic strength of the mixture up to about 70° , or by passing oxygen through a solution of quinone in a dilute aqueous solution of slightly more than the calculated quantity of potash, and afterwards adding the alcohol.

If quinol is dissolved in alcohol containing three molecular proportions of potassium hydroxide, and treated with oxygen at $70-75^\circ$, it likewise yields the compound $C_6K_2O_6$.

The aqueous solutions of these potassium derivatives, when mixed with an acid, yield a black precipitate which is under investigation.

These results indicate that only two of the hydrogen atoms in quinone can be displaced by a metal, and hence afford further evidence of the diketonic character of quinone.

C. H. B.

Action of Sodium Alkyl oxides on Chloranil. Acetals derived from Substituted Quinones. By C. LORING JACKSON and H. S. GRINDLEY (*Amer. Chem. J.*, 1895, **17**, 633—658; compare this vol., i, 19).—*Dichlorodiethoxyquinone tetrethylacetal*, $C_6Cl_2(OEt)_6$, is formed in small quantity by the action of ethylic iodide on silver dichlorodiethoxyquinone hemiacetal; after the dichlorodiethoxyquinone has been removed by treatment with dilute alcoholic soda, the acetal crystallises from light petroleum in large white, rhombic prisms or quadratic plates: it melts at $101-102^\circ$, and sublimes at $260-275^\circ$ without decomposing. When heated with sulphuric acid (sp. gr. = 1.44), it is hydrolysed, dichlorodiethoxyquinone and, in small quantity, chloranilic acid being formed. More dilute acid, alkali, either aqueous or alcoholic, and bromine are without action on the acetal. *Dichlorodiethoxyquinone dibenzoyldiethylacetal*, $C_6Cl_2(OEt)_4(OBz)_2$, is obtained by the action of benzoic chloride on the sodium salt of the hemiacetal suspended in alcohol; it is not formed in presence of ether, nor by the action of benzoic chloride alone at 100° on either the hemiacetal or the sodium

salt. The yield is about 66 per cent. of the theoretical. The compound crystallises in short, thick, colourless prisms, melts at 170° , does not react with soda, hydroxylamine, or zinc dust and glacial acetic acid.

Hydroxylamine hydrochloride and dichlorodiethoxyquinone readily combine, forming a black crystalline compound. When the above acetal is heated with sulphuric acid (sp. gr. = 1.44), a compound is formed which is probably the oxide of *dichlorodiethoxyquinone dibenzoate*, $C_6Cl_2O(OEt)_2(OBz)_2$, or that of *dichloroquinone benzoyl-diethylacetal*; it crystallises in well-developed hexagonal prisms, melts at 142° , and, with aniline, gives two or more compounds which will be described later. When reduced with hydriodic acid, a compound, $OH \cdot C_6Cl_2(OEt)(OBz)_2$, is formed; this crystallises in prisms, melts at 164° , and is being further investigated. *Dichlorodiethoxyquinol dibenzoate*, $C_6Cl_2(OEt)_2(OBz)_2$, prepared from sodium dichlorodiethoxyquinol and benzoic chloride, crystallises in long prisms, melts at 215° , and dissolves in hot concentrated sulphuric acid, but is not changed by hydrochloric acid, nitric acid, or alkali.

Dichlorodimethoxyquinone dibenzoyldimethylacetal,



prepared like the corresponding ethoxy-derivative (see above), crystallises in colourless plates, melts at 193° , and, when heated with dilute sulphuric acid, yields the oxide of *dichlorodimethoxyquinol dibenzoate*, $C_6Cl_2(OMe)_2(OBz)_2O$, which crystallises in rhombic prisms, melting at $205-206^{\circ}$. *Dichlorodiethoxyquinone diethylacetal ethylic dicarbonate*, $C_6Cl_2(OEt)_4(OCOEt)_2$, prepared from the sodium salt of the hemiacetal and ethylic chlorocarbonate, crystallises in colourless, flat prisms melting at $122-123^{\circ}$.

Tetraphenoxyquinone, $C_6(OPh)_4O_2$, is readily obtained from dichlorodiphenoxyquinone and potassium phenoxide in aqueous solution; it is also formed from potassium phenoxide and chloranil in aqueous solution, and from sodium phenoxide and dichlorodiphenoxyquinone suspended in benzene, but in presence of alcohol, the diethoxydiphenoxy-derivative is obtained; it crystallises from benzene in red prisms, and melts at $229-230^{\circ}$. It is not changed by sulphurous acid at 100° , nor by sulphuric acid (sp. gr. = 1.44); hydriodic acid and stannous chloride in acid solution reduce it slowly, and it dissolves in concentrated sulphuric acid (sp. gr. = 1.83). *Diphenoxy-anilic acid*, $C_6(OPh)_2(OH)_2O_2$, formed by heating the preceding compound with soda (1 : 4), crystallises in thick, lustrous, dark reddish-brown rectangular plates, softens at about 270° , and melts at about 276° . Acids are without action on it. The sodium salt forms black crystals which dissolve in water yielding a purple coloured solution.

Tetraphenoxyquinol, $C_6(OPb)_4(OH)_2$, is obtained when tetraphenoxyquinone is reduced by means of zinc dust and glacial acetic acid; it crystallises in colourless, well developed, thick, rhombic plates, commences to decompose at 210° , and melts at $219-220^{\circ}$. *Diethoxydiphenoxyquinone*, $C_6(OEt)_2(OPh)_2O_2$, is formed from dichlorodiphenoxyquinone and sodium phenoxide in absolute alcoholic solution (see above); it crystallises in long, silky, orange-yellow

stellate needles, and melts at 128° . The yield is poor. *Dimethoxydiphenoxyquinone*, $C_6(OMe)_2(OPh)_2O_2$, prepared from tetraphenoxiquinone and sodium methoxide, crystallises in long, golden-yellow, prismatic needles, and melts at 171° . It is soluble in dilute soda; with sodium methoxide dissolved in methylic alcohol, it becomes white, dissolves in water, and, on the addition of dilute acid, a white, amorphous precipitate is produced which soon decomposes. A hemiacetal is probably formed, but it is much less stable than that derived from the dichloroquinone. *Dibromodiphenoxyquinone*, $C_6Br_2(OPh)_2O_2$, is prepared by the interaction of sodium phenoxide and bromanil in alcoholic solution, but probably an aqueous solution would be preferable; it crystallises in short, blunt, orange-red needles, melts at $266-267^{\circ}$, and is reduced by zinc dust and glacial acetic acid to the colourless quinol. Towards acids it is stable. Bromanil reacts with sodium phenoxide in alcoholic solution like chloranil in aqueous solution.

Dibromodimethoxyquinone dimethylhemiacetal, $C_6Br_2(OMe)_4(OH)_2$, formed from dibromodiphenoxyquinone and sodium methoxide, is white, amorphous, and melts at $178-188^{\circ}$; as it then becomes red, it is probably converted into dibromodimethoxyquinone; the same change is produced by dilute sulphuric acid or dilute hydrochloric acid.

Chlorodiphenoxyquinone, $C_6HCl(OPh)_2O_2$, is formed by the action of potassium phenoxide on trichloroquinone in aqueous solution; it crystallises in long, slender, oval, orange-coloured plates, melts at $169-170^{\circ}$, and, when treated with sodium methoxide, water, and dilute acid successively, it yields an unstable hemiacetal. Sodium ethoxide in alcoholic solution, when mixed with quinone dissolved in ether, gives a heavy, flocculent, dark green precipitate, which is decomposed by alcohol and water; when dried in air, it ignites spontaneously at the ordinary temperature, but if dried in hydrogen, and then exposed to air, it is stable up to 40° , but then burns like tinder; it is not a homogeneous substance, and in its production the constituents react in molecular proportion. The same compound, together with phenol, appears to be formed by the action of sodium ethoxide on phenoquinone. In order to ascertain whether phenoquinone is a hemiacetal, the action of sodium phenoxide on quinone was investigated; in presence of light petroleum a dark green precipitate is formed; with benzene as solvent, the precipitate is pink, and becomes dark green when heated; in ethereal solution, a dark red, crystalline compound is deposited; after removal of the ether, the residue readily dissolves in water with a slight green colour, and, when acidified, a dark red, crystalline substance is precipitated in small quantity. The subject is still under investigation.

J. B. T.

Action of Bromine on Metanitriline. By HENRY L. WHEELER (*Amer. Chem. J.*, 1895, **17**, 697—704).—The chief product formed by the action of bromine, in glacial acetic acid solution, on metanitriline is *bromonitriline* [$NH_2 : NO_2 : Br = 1 : 3 : 6$], which crystallises in bright yellow needles melting at $139-140^{\circ}$. Its constitution is shown by the formation of parabromonitrobenzene

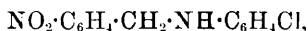
when it is treated with ethylic nitrite, and of dibromonitrobenzene [$\text{NO}_2 : \text{Br} : \text{Br} = 1 : 3 : 4$] by means of Sandmeyer's reaction. The compound is volatile with steam, is less basic than the isomeride [$\text{NH}_2 : \text{NO}_2 : \text{Br} = 1 : 3 : 4$], and, with strong acids, forms salts which are decomposed by water. The yield is 87.5 per cent. of the nitraniline employed; and by using metanitracetylanilide, this is increased to 111 per cent. The *hydrochloride* crystallises in colourless, lustrous scales melting and decomposing at about 200° . The *sulphate* is deposited in broad, thin, colourless, lustrous plates. The *acetyl derivative* crystallises in colourless, silky needles melting at 180° . Tribromonitraniline [$\text{NH}_2 : \text{NO}_2 : \text{Br}_3 = 1 : 3 : 2 : 4 : 6$] is formed together with the preceding compound; the yield is 19 and 107 per cent. of the aniline and acetanilide respectively. Aniline, under the above conditions, yields chiefly di- and tri-bromo-derivatives, and when monobromo-derivatives are formed, they are para- and not principally ortho-compounds; in this instance, therefore, the nitro-group in the meta-position exerts a protective influence, and affects the position of the substituting atoms.

J. B. T.

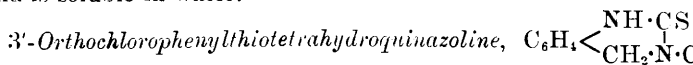
A Correction (Bromination of Acetanilide and Acetoparatoluidide). By WILHELM VAUREL (*Ber.*, 1895, 28, 3059).—The author points out that his observation regarding the bromination of acetanilide and acetoparatoluidide (*Abstr.*, 1894, i, 19) is identical with that recorded by Blacher (*Ber.*, 1895, 28, 2359).

M. O. F.

Orthamidobenzylamine. By MAX BUSCH (*J. pr. Chem.*, 1895, [2], 52, 373—416; compare *Abstr.*, 1895, i, 306—307).—X. With F. BRUNNER.—*Orthonitrobenzylorthochloraniline*,



is prepared by heating orthonitrobenzyl chloride with orthochloraniline (2 mols.) for five hours in alcoholic solution, and is precipitated by adding water to the solution. It crystallises in yellow needles, melts at 67° , and dissolves easily in the usual solvents; the *hydrochloride* forms white needles, and melts at 172° . By reduction with zinc and acetic acid, the nitro-compound yields *orthamidobenzylorthochloraniline*, which crystallises in aggregates of yellowish needles, melts at 58° , and dissolves readily in ether and benzene, and in warm alcohol; the *hydrochloride* forms colourless needles, melts at 152° , and is soluble in water.



(*Abstr.*, 1894, i, 146), crystallises in white, silky laminae, which become reddish on exposure to light, melt at 200° , and dissolve sparingly in the usual solvents. Reduction by means of sodium in alcohol converts it into 3-phenyltetrahydroquinazoline, and oxidation by mercuric oxide in alcohol at 150° converts it into 3'-orthochlorophenylketotetrahydroquinazoline, $\text{C}_6\text{H}_4 < \begin{array}{c} \text{N} - \text{CO} \\ | \\ \text{CH}_2 \cdot \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{Cl} \end{array}$, which crystallises in colour-

less laminæ, melts at 207° , and dissolves in alcohol and, sparingly, in ethylic acetate.

XI. With FRANCIS E. FRANCIS.—*Orthonitrobenzylmetachloraniline* forms yellow crystals, melts at 59° , and dissolves easily in glacial acetic acid, alcohol, ether, and benzene, but sparingly in light petroleum, and not at all in water. *Orthamidobenzylmetachloraniline* is an oil; its *hydrochloride* crystallises in white laminæ, melts at 137 – 138° , and is sparingly soluble in water, although freely soluble in alcohol.

Metachlorophenylindazole, $C_6H_4 \begin{smallmatrix} N- \\ | \\ CH \end{smallmatrix} > N \cdot C_6H_4Cl$, also produced

during the reduction of orthonitrobenzylmetachloraniline, crystallises in large, white laminæ, melts at 110° , and dissolves easily in ether, benzene, and chloroform, but only sparingly in cold alcohol.

3'-Metachlorophenylthiotetrahydroquinazoline crystallises in colourless, vitreous needles, melts at 198 – 199° , and is sparingly soluble save in glacial acetic acid and chloroform; reduction only affects the chlorine, *3'-phenylthiotetrahydroquinazoline* being formed.

Metachlorophenyldihydro- β -phenotriazine, $C_6H_4 \begin{smallmatrix} N=N \\ | \\ CH_2 \cdot N \cdot C_6H_4Cl \end{smallmatrix}$

prepared by the action of amylic nitrite on an alcoholic solution of orthamidobenzylmetachloraniline hydrochloride, crystallises in yellow needles, melts and evolves gas at 146 – 147° , and dissolves easily in benzene, ether, and hot alcohol, sparingly in light petroleum.

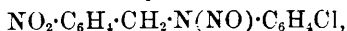
XII. With C. VOLKENING.—*Orthonitrobenzylparachloraniline* has been already described (Abstr., 1894, i, 210); the *hydrochloride* melts at 170 – 172° ; the *sulphate* is described. *Orthamidobenzylparachloraniline* crystallises in lustrous, white needles, melts at 89 – 90° , and is freely soluble in most organic solvents; a *hydrochloride* and a *dihydrochloride* are described.

The *benzylidene* derivative, $CHPh \cdot N \cdot C_6H_4 \cdot CH_2 \cdot NH \cdot C_6H_4Cl$, formed by heating orthamidobenzylparachloraniline with benzaldehyde in alcohol, crystallises in stellate groups of white needles, melts at 115 – 116° , and dissolves easily in hot benzene and alcohol, but only sparingly in ether or light petroleum. The *orthohydroxybenzylidene* derivative crystallises in stellate groups of yellow prisms, melts at 124° , and is soluble in the usual solvents. The *metanitrobenzylidene* derivative melts at 86° , and is sparingly soluble in alcohol, ether, and chloroform, more so in benzene and glacial acetic acid, and insoluble in light petroleum. *Orthacetamidobenzylparachloraniline*, $NHAc \cdot C_6H_4 \cdot CH_2 \cdot NH \cdot C_6H_4Cl$, prepared by heating the base with acetic anhydride, crystallises in long, colourless prisms, melts at 188° , and dissolves freely in hot benzene, chloroform, and carbon bisulphide.

3'-Parachlorophenylthiotetrahydroquinazoline crystallises in lustrous, white laminæ, melts at 228° , and is soluble in the usual solvents, except carbon bisulphide and boiling glacial acetic acid. *Parachlorophenyldihydro- β -phenotriazine* crystallises in yellow laminæ, and also in thick crystals; it melts at 134° , and dissolves easily in benzene and chloroform, but only sparingly in ether or light petroleum; the

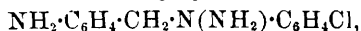
hydrochloride, $C_{13}H_{10}N_3Cl.HCl$, melts and explodes at 103° , and is soluble in alcohol, but is dissociated by water; the *platinochloride*, *aurochloride*, and *picrate* are described.

Parachlorophenylorthonitrobenzylnitrosamine,



crystallises in yellow, transparent prisms, melts at 100° , and dissolves freely in benzene, glacial acetic acid, and hot alcohol, but only sparingly in ether or light petroleum.

Parachlorophenylorthamidobenzylhydrazine,



forms crystals, and melts at 95° ; it dissolves in most solvents, and yields a *benzylidene* derivative, $CHPh:N \cdot C_6H_4 \cdot CH_2 \cdot N(N:CHPh) \cdot C_6H_4Cl$, when heated with benzaldehyde and alcohol; this crystallises in long, felted needles, melts at 150° , and dissolves easily in ether, benzene, carbon bisulphide, and chloroform, but only sparingly in alcohol.

XIII. With FR. HEINEN.—Orthamidobenzylparabromaniline has been already described (Abstr., 1894, i, 210); the *dihydrochloride* melts at 93 – 94° , and the *oxalate* at 127° ; the *benzylidene* derivative (*benzylideneorthamidobenzylparabromaniline*) crystallises in stellate groups of white needles, melts at 122° , and dissolves freely in chloroform, carbon bisulphide, and glacial acetic acid, but only sparingly in ether, alcohol, benzene, or light petroleum; the *ortho*hydroxybenzylidene derivative crystallises in yellow prisms, melts at 143 – 144° , and is soluble in most solvents; the *para*nitrobenzylidene derivative melts at 144° , and is sparingly soluble in the usual solvents, except glacial acetic acid and benzene. *Orthacetamidobenzylparabromaniline* crystallises in colourless prisms, melts at 138° ; it is easily soluble in benzene and chloroform, but very sparingly in ether and light petroleum.

3'-Parabromophenylketotetrahydroquinazoline, from carbonyl chloride and orthamidobenzylparabromaniline, crystallises in transparent, quadratic tablets, melts at 226° , and is sparingly soluble in alcohol, ether, carbon bisulphide, and light petroleum, but freely in boiling benzene, glacial acetic acid, and chloroform. *Parabromophenylthio-tetrahydroquinazoline* forms long, colourless, four-sided prisms, melts at 234° , and dissolves easily in amyl alcohol.

Parabromophenyldihydro- β -phenotriazine crystallises in lustrous, yellow laminae, melts at 164° , and dissolves freely in benzene, alcohol, ether, chloroform, and carbon bisulphide, sparingly in light petroleum, and not at all in water; the *hydrochloride* melts at 105 – 106° ; the *platinochloride* (m. p. 191°), *aurochloride* (m. p. 108 – 109°), and *picrate* (m. p. 106°), are described.

Parabromophenylorthonitrobenzylnitrosamine,



formed by the action of nitrous acid on orthonitrobenzylparabromaniline, crystallises in microscopic tables, melts at 167° , and dissolves easily in the usual solvents, except light petroleum. *Parabromophenylorthamidobenzylhydrazine* crystallises in lustrous tables, melts at 119 – 120° , and dissolves freely in the usual solvents, except light

petroleum; the *oxalate* melts at 135° ; the *benzylidene* derivative, $\text{CHPh}\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{N}(\text{N}\cdot\text{CHPh})\cdot\text{C}_6\text{H}_4\cdot\text{Br}$, crystallises in long, colourless prisms, melts at 171° , and dissolves in most solvents.

XIV. With PAUL HARTMANN. — *Orthamidobenzylparaphenetidine*, from orthonitrobenzylparaphenetidine (*loc. cit.*), crystallises in nacreous laminæ, melts at 78° , and dissolves in alcohol, ether, benzene, chloroform, and glacial acetic acid; the *hydrochloride*, *sulphate* (m. p. 100°), *oxalate* (m. p. 132°), *benzylidene* derivative (m. p. 137°), and *orthohydroxybenzylidene* derivative (m. p. 94°), are described.

3'-Phenetylketotetrahydroquinazoline, $\text{C}_6\text{H}_4\cdot\begin{smallmatrix} \text{NH}\cdot\text{CO} \\ | \\ \text{CH}_2\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{OEt} \end{smallmatrix}$, crystallises in colourless needles, and melts at 223° ; it dissolves in glacial acetic acid, ethylic acetate, and chloroform, sparingly in ether and benzene, and not at all in water or light petroleum. *3'-Phenethylthiotetrahydroquinazoline* crystallises in white, silky needles, melts at 238° , and dissolves sparingly in the usual organic solvents, but not in ether, light petroleum, or water. *3'-Paraphenetyltetrahydroquinazoline* melts at 129° , not 124° (*loc. cit.*).

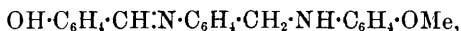
Paraphenetyldihydro- β -phenotriazine crystallises in yellow laminæ, melts at 144° , and is soluble in the usual solvents, except light petroleum; the *hydrochloride* (m. p. 115°), *platinochloride*, *aurochloride*, *hydrobromide* (m. p. 104°), and *picrate* are described.

XV. With F. BRUNNER and RUD. BIRK. — *Orthonitrobenzylorthanisidine*, $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{OMe}$, forms brilliant, thick, orange-red crystals, and melts at 80° .

Orthamidobenzylorthanisidine crystallises in colourless needles, and melts at 99° ; the *dihydrochloride* melts at $175\text{--}176^{\circ}$.

Azo-orthobenzylorthanisidine, $(\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4)_2\text{N}_2$, crystallises in orange needles, melts at $150\text{--}151^{\circ}$, and dissolves easily in benzene, sparingly in ether.

Orthohydroxybenzylideneorthamidobenzylorthanisidine,



from salicylaldehyde and orthamidobenzylorthanisidine, crystallises in yellow, silky needles, and melts at 79° .

3'-(Orthomethoxyphenylketotetrahydroquinazoline melts at $217\text{--}218^{\circ}$, and *3'-(Orthomethoxyphenylthiotetrahydroquinazoline* at 237° .

XVI. With PAUL HARTMANN. — *Orthamidobenzylparanisidine* melts at 82° ; *paranisylidihydro- β -phenotriazine* melts at 139° ; both dissolve in most solvents; the *hydrochloride*, *platinochloride*, and *picrate* (m. p. 125°) of the triazine are described.

XVII. With FR. BRAND. — *Orthamidobenzyl- α -naphthylaminu*,



crystallises in lustrous, reddish laminæ, melts at 134° , and dissolves in benzene easily, and in alcohol, ether, and light petroleum with difficulty; the solutions have a bluish-red fluorescence; the *dihydrochloride*, the *sulphate*, $\text{C}_{17}\text{H}_{16}\text{N}_2(\text{H}_2\text{SO}_4)_2$, the *benzylidene* derivative (m. p. 107°), and the *orthohydroxybenzylidene* derivative (m. p. 162°) are described.

3'- α -Naphthylthiotetrahydroquinazoline crystallises in colourless,

lustrous laminæ, melts at 255° , and dissolves easily in xylene, amyl alcohol, and chloroform; the 1'-methyl derivative, $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{NMe} \cdot \text{CS} \\ | \\ \text{CH}_2 \cdot \text{N} \cdot \text{C}_{10}\text{H}_7 \end{smallmatrix}$, formed by the action of methylic iodide on the quinazoline, crystallises in white needles; its hydriodide blackens and melts at 212° .

XVIII. With FR. BRAND.—*Orthonitrobenzyl-β-naphthylamine*, from β-naphthylamine and orthonitrobenzyl chloride, crystallises in lustrous, red laminæ, melts at 162° , and dissolves in the usual solvents, save chloroform; the hydrochloride is described. *Orthamidobenzyl-β-naphthylamine* forms white, lustrous laminæ, melts at 99° , and dissolves like the α-compound; the benzylidene derivative (m. p. 122°), *orthohydroxybenzylidene* derivative (m. p. 117°), and methylene derivative (m. p. 155 – 158°) are described. *Orthoacetamidobenzyl-β-acetonaphthalide*, $\text{NHAc} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{NAc} \cdot \text{C}_{10}\text{H}_7$, forms colourless, thick crystals, melts at 116° , and dissolves sparingly in ether, benzene, and glacial acetic acid, but not in light petroleum.

3'-β-Naphthylthiotetrahydroquinazoline crystallises in thick, colourless laminæ, melts at 280° , and dissolves freely in glacial acetic acid and amyl alcohol; the 1'-methyl derivative melts at 140° , and its hydriodide decomposes and melts at 249° .

Orthonitrobenzyl-β-naphthylnitrosamine crystallises in dark yellow, thick laminæ, melts at 102° , and dissolves freely in benzene, glacial acetic acid, and chloroform. *Orthamidobenzyl-β-naphthylhydrazine*, prepared by the reduction of the nitrosamine, crystallises in slender needles, and melts at 76° ; its *orthohydroxybenzylidene* derivative, $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{CH} \cdot \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{N}(\text{N} \cdot \text{CH} \cdot \text{C}_6\text{H}_4 \cdot \text{OH}) \cdot \text{C}_{10}\text{H}_7$, crystallises in yellow, felted needles, melts at 176° , and dissolves freely in benzene, glacial acetic acid, and chloroform. A. G. B.

Derivatives of Dimethylparatoluidine. By JOHANNES PINNOW (*Ber.*, 1895, 28, 3039–3045; compare *Abstr.*, 1895, i, 98).—*Orthonitroparatolylmethylnitrosamine* is obtained by adding aqueous sodium nitrite to orthonitrodimethylparatoluidine dissolved in hydrochloric acid; it crystallises from alcohol in yellow needles or prisms, and melts at 55° . *Orthonitromethylparatoluidine* is formed when methylparatoluidine is nitrated in sulphuric acid solution, the liquid being subsequently treated with sodium nitrite at 0° ; it crystallises in red needles or prisms, melting at 57° , and the acetyl derivative crystallises in slender, yellow needles melting at 128 – 128.5° . *Methylorthonitroparatolylnitramine* is isolated from the liquid containing orthonitroparatolylmethylnitrosamine; it crystallises from acetone in red prisms with green reflex, and melts at 184.5 – 185.5° (uncorr.). An ethereal extract of the liquid, when treated with sodium carbonate, yields *dinitrodimethylparatoluidine*, which crystallises from alcohol in red, lustrous leaflets, and melts at 103.5 – 104° .

Metanitrodimethylparatoluidine is also formed by the action of nitrous acid on dimethylparatoluidine, and is obtained as a dark red oil, which does not solidify at -15° . *Amidodimethylparatoluidine*, produced when the nitro-compound is reduced with tin and hydrochloric acid, is a colourless oil, which boils at 234° (uncorr.) under a pressure of 759 mm.; the hydrochloride and mercurichloride

melt at 192—193° and 205—206° respectively, whilst the *picrate* crystallises from alcohol in brownish-yellow prisms, and melts at 150·5°. The action of boiling acetic anhydride during four hours converts the base into methylethenyltolulylenamidine (Niementowski, Abstr., 1887, 937); the *acetyl* derivative of amidodimethylparatoluidine is obtained by the action of glacial acetic acid during eight hours, and melts at 111·5—112·5°. The *phenylthiocarbamide* crystallises in prisms, and melts at 153—154° (uncorr.).

In addition to amidodimethylparatoluidine, reduction of metanitrodimethylparatoluidine gives rise to a *compound* which crystallises in white needles, and yields a *picrate*, crystallising from amyl alcohol in yellow leaflets, and melting at 254·5° (uncorr.).

When nitrous gas is led into a solution of dimethylparatoluidine in nitric acid, methyl dinitro tolylnitrosamine (Gattermann, Abstr., 1885, 975) is formed; it is also obtained by the action of nitric acid on methyltolyl nitrosamine dissolved in glacial acetic acid.

M. O. F.

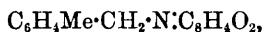
Synthetical Use of Iodine Chloride. By M. KERSCHBAUM (*Ber.*, 1895, 28, 2798—2804).—*as*-Metaxylylidine is converted by 1 mol. of iodine chloride, ICl, into *orthoiodometaxylylidine*, $[\text{Me}_2 : \text{NH}_2 : \text{I} = 1 : 3 : 4 : 5]$; the base crystallises in colourless needles, melting at 65°. The *hydrochloride* is only sparingly soluble in water, whilst the *nitrate* and *sulphate* are more readily soluble. The *acetyl* compound forms lustrous white plates melting at 85°. The *nitrile* crystallises in yellowish needles, and melts at 135°. It has not yet been found possible to convert this substance by hydrolysis into an acid.

When 2 mols. of iodine chloride react with metaxylylidine, the iodo-derivative is accompanied by a small amount of *tetramethylortho-diamidodiphenyl* $[\text{Me}_4 : (\text{NH}_2)_2 = 3 : 5 : 3' : 5' : 2 : 2']$, which is formed from the xylylidine by condensation. It crystallises in small, rhombic tablets, melts at 180°, and may be distilled in small quantities, almost without decomposition. The *hydrochloride* and *sulphate* are readily soluble; the *nitrate* is sparingly soluble, and crystallises in large, white prisms. The *diacetyl* compound forms small plates, and melts at 210°. The base can readily be diazotised, and yields colouring matters with α - and β -naphthol, &c. *Tetramethyldiphenylimide* (tetramethylcarbazole), $\text{C}_6\text{H}_2\text{Me}_2 \langle \text{NH} \rangle \text{C}_6\text{H}_2\text{Me}_2$, is formed when the tetrazo-solution is treated with potassium sulphide. It crystallises in small plates, melts at 128—129°, and, like carbazole, forms a yellow solution in sulphuric acid, turned green by nitric acid. It is insoluble in water, but readily soluble in alcohol, &c. The *picrate* forms reddish-brown needles.

No analogous compounds have been obtained from other bases by the action of 2 mols. of iodine chloride.

A. H.

Amido-derivatives of Paraxylylene. By FRANZ LUSTIG (*Ber.*, 1895, 28, 2986—2994).—Paramethylbenzylphthalimide,



and paraxylylene-exo-diphthalimide were obtained by treating with

potassium phthalimide the mixture of mono- and di-bromoparaxylenes with the dibromide [$\text{C}_6\text{H}_4\text{Me}\cdot\text{CH}_2\text{Br}$ and $\text{C}_6\text{H}_4(\text{CH}_2\text{Br})_2$] obtained by the bromination in sunlight of cold paraxylene; they were separated by extraction with cold carbon bisulphide in which the monophthalimide alone is soluble. The monophthalimide yields paramethylbenzylphthalamic acid when hydrolysed with alcoholic potash, and paramethylbenzylamine when hydrolysed with a mixture of acetic and concentrated hydrochloric acids at $150\text{--}160^\circ$. Paramethylbenzylamine picrate melts at 204° (Kröber, Abstr., 1890, 968, gives $194\text{--}199^\circ$), the acetyl derivative at $107\text{--}108^\circ$ (Kröber, 106.5°), and the benzoyl compound at 137° (Kröber, 125°).

Metanitroparamethylbenzylbenzamide, $\text{NO}_2\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{CH}_2\cdot\text{NHBz}$, is obtained when the above benzoyl derivative is dissolved in sulphuric acid, and then treated with a mixture of nitric and sulphuric acids. It crystallises in colourless needles, melts at $145\text{--}147^\circ$, and when hydrolysed with hydrochloric acid, yields benzoic acid and *nitroparamethylbenzylamine hydrochloride*; the *platinochloride*,



forms an orange red, crystalline powder, and decomposes at 231° ; the *picrate* crystallises in short, bright yellow needles, and melts and decomposes at 211° .

The benzoyl compound, when reduced with zinc and hydrochloric acid, according to Gabriel and Jansen's method (Abstr., 1890, 1442), yields *metamidoparamethylbenzylbenzamide*, which crystallises from water in colourless needles, and melts at $113\text{--}115^\circ$. Since it is not converted into an anhydride by heating to 300° , nor by distillation, it is probable that the amide group is not in the ortho-position relatively to the $\text{CH}_2\cdot\text{NHBz}$ -group. The amido-compound must therefore be $\text{NH}_2\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{CH}_2\cdot\text{NHBz}$ [= 3 : 4 : 1]. The *hydrochloride* decomposes and melts at 237° , the *picrate* turns brown, and melts at $170\text{--}171^\circ$, and the *chromate* forms yellowish-red needles, which decompose at 80° . The benzoyl compound, when hydrolysed with hydrochloric acid at 150° , yields *metamidoparamethylbenzylamine hydrochloride*; this crystallises in colourless needles, melts with decomposition at 285° , and yields a *picrate*, which also decomposes at 285° .

Paraxylylene-exo-diphthalimide, $\text{C}_6\text{H}_4(\text{CH}_2\cdot\text{N}\cdot\text{C}_6\text{H}_4\text{O}_2)_2$, is insoluble in alcohol, ether, chloroform, benzene, and acetic acid, but crystallises from nitrobenzene in small, white needles; it melts at $279\text{--}280^\circ$, and, when hydrolysed with alcoholic potash, yields *paraxylylene-exo-diphthalamic acid*, $\text{C}_6\text{H}_4(\text{CH}_2\cdot\text{NH}\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{COOH})_2$, which, when heated to 279° , loses water, and is converted back again into the diphthalimide.

Nitroparaxylylene-exo-diphthalimide crystallises from nitrobenzene in colourless needles, and melts at $253\text{--}255^\circ$.

Paraxylylene-exo-diamine hydrochloride, $\text{C}_6\text{H}_4(\text{CH}_2\cdot\text{NH}_2\cdot\text{HCl})_2 + 1\frac{1}{2}\text{H}_2\text{O}$, obtained by the hydrolysis of the diphthalimide with concentrated hydrochloric acid, crystallises in colourless needles; the *platinochloride* decomposes at 250° , and the *picrate*, which crystallises in large, orange needles, at 232° .

The *tetracetyl derivative*, $C_6H_4(CH_2.NAc)_2$, crystallises in colourless needles and melts at 194° , and the *dibenzoyl derivative* at $193-194^\circ$.

Nitroparaxylylene-exo-diamine hydrochloride, obtained from the nitroparaxylylene-exo-diphtalimide, crystallises with $1\frac{1}{2}H_2O$, and decomposes when heated for some time at 160° . The *platinochloride* decomposes at 295° , and the *picrate* at 237° .

Nitroparaxylylene-exo-dibenzamide, obtained by the action of benzoic chloride on the nitro-base, crystallises in colourless needles, and melts at $210.5-211^\circ$. J. J. S.

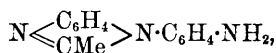
Amido-derivatives of Diphenylamine and their relation to Indamines and Azines. By RUDOLF NIETZKI (*Ber.*, 1895, 28, 2969-2981).—I. With KARL ALMENRÄDER.—2 : 4-Dinitrodiphenylamine, $NHPh \cdot C_6H_3(NO_2)_2$, is best reduced by iron filings and 2 per cent. hydrochloric acid, the liquid being finally treated with excess of sodium carbonate. The diamido-compound forms brownish needles and melts at 130° ; its salts are very unstable; it does not condense to an azine, exhibits the behaviour of a meta-diamine, and yields a colourless *diacetyl derivative* melting at 188° . Warm alcoholic ammonium sulphide reduces the dinitro-compound partially to red *nitramidodiphenylamine*, $NHPh \cdot C_6H_3(NH_2) \cdot NO_2$ [1 : 2 : 4]; this melts at 125° , and yields a *monacetyl derivative* melting at $163-164^\circ$. Nitrous acid converts it into a yellowish *azimide*, $NO_2 \cdot C_6H_3 < \begin{smallmatrix} NPh \\ N \end{smallmatrix} > N$, which melts at 107° , and can be reduced with stannous chloride to the colourless *amido-derivative*, which melts at 159° and forms a *platinochloride*, and a *monacetyl derivative* melting at 266° .

II. With CARL SIMON.—1 : 2 : 4-Diamidodiphenylamine is oxidised by manganese dioxide in very dilute ammoniacal solution to a yellowish-brown compound, $C_{12}H_{10}N_2O$, of undetermined constitution, melting at 152° .

2 : 4-Dinitro-4'-hydroxydiphenylamine, $C_6H_3(NO_2)_2 \cdot NH \cdot C_6H_4 \cdot OH$, was prepared by the action of paramidophenol on dinitrochlorobenzene; it is red, and melts at 190° ; its yellow *monacetyl derivative* melts at 129° . It can be reduced by stannous chloride to the *diamido-compound*, which forms a rather unstable *monohydrochloride* and readily oxidises in the presence of air to the dark-coloured diamidoindophenol, $C_6H_3(NH_2)_2 \cdot N : C_6H_4 \cdot O + 2H_2O$ [$(NH_2)_2 : OH = 2 : 4 : 4'$], which melts at 133° when anhydrous. If the hydrochloride is oxidised with manganese peroxide, yellow *amidohydroxyphenazine*, $NH_2 \cdot C_6H_3 < \begin{smallmatrix} N \\ | \\ N \end{smallmatrix} > C_6H_3 \cdot OH$ [$NH_2 : OH = 3 : 3'$], is obtained; this melts at 268° , its greenish-yellow *diacetyl derivative* at 258° . 2 : 4-Diamido-2'-hydroxydiphenylamine was prepared by reducing the corresponding dinitro-compound; it was not isolated on account of its extreme instability, but was at once oxidised, when it yielded O. Fischer and Hepp's red 3-amidophenazine, $NH_2 \cdot C_6H_3 < \begin{smallmatrix} N \\ | \\ N \end{smallmatrix} > C_6H_4$, melting at 265° .

III. With OTTO BAUR.—The red dinitrodiphenylamine obtained by

Witt (*Ber.*, 11, 758) is shown to be the 2:4'-dinitro-compound, $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$. It can be made from 1:4-mononitrodiphenylamine, and so contains one nitro-group in the para-position; that the second is in the ortho-position is shown by the conversion into a phenazine, and other reactions described below. Partially reduced, it yields a nitramido-compound, which is reddish-brown with a shimmer of blue, and melts at 144° ; this yields a yellow *monacetyl derivative* melting at 178° ; with nitrous acid, it yields a yellow *nitroazimide* melting at 239° , that can be reduced with stannous chloride to a colourless *amido-compound* melting at $134\cdot5^\circ$, the *mon-acetyl derivative* of which melts at 200° . The diamido-compound obtained by complete reduction of dinitrodiphenylamine (Nietzki and Witt, *Ber.*, 12, 1399) readily oxidises to the red amidophenazine melting at 265° . Its acetyl derivative, when heated at 120° with strong hydrochloric acid, does not regenerate the diamido-base, as was formerly supposed, but yields the *ethenyl derivative*,



the acetyl derivative of which melts at 219° .

IV. The following general conclusions are drawn as to the behaviour of the amidodiphenylamines. (1) To get an indamine, the para-positions in both benzene nuclei must be occupied. (2) Azines are formed when a para-position is occupied in one nucleus, and an ortho-position in the other, and no indamine is then formed as an intermediate product. If one nucleus has no substituting groups, or only one in the meta-position, neither an indamine nor an azine is formed. (3) If the ortho-positions in both nuclei are occupied, one of the occupying groups (NH_2 or OH) is lost when the phenazine is formed.

C. F. B.

Preparation of Orthophenylenediamine. By OSCAR HINSBERG and FRITZ KÖNIG (*Ber.*, 1895, 28, 2947).—Fifty grams of orthonitraniline is dissolved in 100–150 c.c. of boiling alcohol, 40 c.c. of 20 per cent. aqueous caustic soda added, and then zinc dust is introduced fairly rapidly in small portions at a time. When the addition of zinc dust seems to produce no further action, 10 c.c. more caustic soda is added, and the addition of zinc dust continued as before; this proceeding should be repeated once or twice. In about an hour, the reddish-yellow colour of the solution will have changed to a pale brown, and the action will be complete. The solution is then filtered, the residue extracted twice with boiling alcohol, and the filtrate and washings evaporated in a current of hydrogen until all the alcohol has been driven off. The residue of orthophenylenediamine is broken up when cold, dried on a porous plate, and distilled; the yield is 90 per cent. of the theoretical. Other amidonitro-compounds can be reduced conveniently in the same manner; not, however, alkyl derivatives of orthonitraniline.

C. F. B.

Action of Ethylic Orthoformate on Primary Aromatic Amines. By R. WALTHER (*J. pr. Chem.*, 1895, [2], 52, 429–430).—

This reaction yields amidines very easily at the temperature of the water bath in the majority of cases (compare Claisen, this vol., i, 91). The following were obtained: *Methenyldiphenylamidine*, silvery laminæ or prisms, m. p. 138—139°. *Methenyldiorthonitrophenylamidine*, brilliant, golden needles, m. p. 124—125°. *Methenyldimetanitrophenylamidine*, soft, felted needles, m. p. 198—199°. *Methenyldiparanitrophenylamidine*, golden laminæ, m. p. 236—237°. *Methenyldiorthotolylamidine*, lustrous, white laminæ, or thick, transparent crystals, m. p. 149°. *Methenyldiparatolylamidine*, white laminæ or large, transparent prisms, m. p. 141°; the acetate crystallises in white needles. *Formazyl hydride*, obtained by the action of ethylic orthoformate on phenylhydrazine, forms violet crystals, m. p. 117°; from light petroleum, it separates as a red, crystalline mass (containing petroleum of crystallisation), which melts at 114°. *Methenyldimetabromophenylamidine*, silvery laminæ or stout prisms, m. p. 135°. *Methenylditribromophenylamidine*, long, white needles, m. p. 78°.

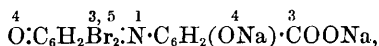
The compound from amidoazobenzene forms long, brownish-red prisms or slender needles, and melts at 191—193°; that with picramic acid is a moss-green powder, melting at 183—184°, and is absolutely insoluble.

A. G. B.

Quinazine and Oxazine Colouring Matters. By RICHARD MÖHLAU and KARL UHLMANN (*Annalen*, 1895, **289**, 90—130; compare Abstr., 1892, 887, and 1893, i, 44).—The authors accept the modification in the nomenclature of these colouring matters which has been put forward by Nietzki and Bossi (*loc. cit.*), and they also adopt the expressions *azime* and *azone* for indamine and indophenol derivatives respectively; thus reference is made to phenylene-blue and α -naphthol-blue as amidodiphenazine and dimethylamidophenonaphthazone.

Dibromodimethylamidodiphenazone, $\text{O}:\text{C}_6\text{H}_2\text{Br}_2:\text{N}:\text{C}_6\text{H}_4\text{NMe}_2$, obtained by adding dimethylaniline (2 mols.) to an alcoholic solution of dibromoquinonechlorimide saturated at 30°, separates in green prisms which appear blue by transmitted light; when heated on platinum foil, it decomposes without undergoing fusion. The dye is insoluble in water, but dissolves sparingly in cold alcohol and ether, yielding greenish-blue solutions, whilst hot alcohol, aniline, and pyridine dissolve it readily. Dimethylamidodibromodiphenazone is hydrolysed by boiling dilute hydrochloric acid, yielding ammonia, dimethylaniline, dibromoparamidophenol, dibromoquinone, and quinone, whilst boiling caustic soda gives rise to hydroxydibromodiphenazone and dimethylaniline.

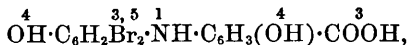
Sodium dibromodiphenazone-orthohydroxycarboxylate,



is obtained on agitating dibromoquinonechlorimide (15 grams) dissolved in ether (300 c.c.) with a solution (135 c.c.) containing 5 grams of salicylic acid and 4.4 grams of caustic soda in 100 c.c. of water; it dissolves readily in water and alcohol, yielding blue liquids, but is insoluble in ether. Concentrated sulphuric acid dissolves it, forming

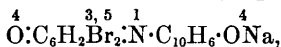
an orange-yellow solution, which becomes purple, and ultimately colourless, on dilution with water. The *acid* is liberated in the form of a brownish-red powder, which dissolves sparingly in water and chloroform, being readily soluble in acetone, alcohol, and ether.

Dibromodihydroxydiphenylaminecarboxylic acid,



the leuco-derivative of the foregoing compound, is obtained from it by reduction with grape sugar or zinc and alkali; it crystallises from acetone in needles, and melts and decomposes at 209°. The substance is insoluble in water and chloroform, dissolving in ether, alcohol, pyridine, and acetone; the solution in caustic soda rapidly undergoes oxidation when exposed to air.

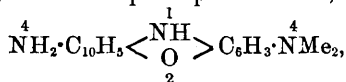
The *sodium* derivative of *dibromohydroxynaphthadiphenazone*,



produced by the action of dibromoquinonechlorimide on an alkaline solution of α -naphthol, crystallises in blue needles with green reflex; it yields a blue solution with water and alcohol, but is insoluble in ether. When the sodium derivative absorbs carbonic anhydride, *dibromohydroxynaphthadiphenazone* is produced; this melts at 201° without decomposing. Hot dilute mineral acids resolve it into dibromoparamidophenol, dibromoquinone, and 1:4-amidonaphthol. *Dibromohydroxyphenylhydroxynaphthylamine*, the leuco-derivative of the foregoing compound, is obtained by reducing it in alcoholic solution with grape sugar and caustic soda; it crystallises in lustrous, white leaflets, and decomposes at 152° without melting.

Dimethylamidophenonaphthoxazime, $\overset{4}{\text{NH}}\cdot\overset{1}{\text{C}_{10}\text{H}_5}\text{<} \overset{2}{\underset{\text{O}}{\overset{\text{N}}{\text{>}}}} \text{C}_6\text{H}_3\cdot\overset{4}{\text{NMe}_2}$, is

prepared by adding nitrosodimethylmetamidophenol hydrochloride (17 grams) to a boiling 10–15 per cent. solution of α -naphthylamine hydrochloride (10 grams) in acetic acid containing 20 per cent. of water; this operation yields the *hydrochloride*, which crystallises from boiling water acidified with a few drops of hydrochloric acid, in small needles; it appears green by transmitted, and violet by reflected light. The dye forms a blue solution in water, alcohol, and pyridine, and the solution in concentrated sulphuric acid is orange-red, becoming green and blue successively on dilution with water; owing to its constitutional relation to the well-known dye, the authors refer to it as “methyl Nile blue.” The *base* is liberated when caustic soda is added to the dye suspended in absolute alcohol until the colour is changed from blue to red; it crystallises in reddish-brown needles which contain water, and become anhydrous at 120°. It decomposes before melting, and yields fluorescent liquids with common organic solvents. Reduction with zinc and hydrochloric acid converts the base into the *zincchloride* of the leuco-derivative, dimethyldiamidonaphthaphenoxazine,

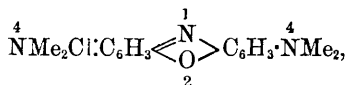


which crystallises in greenish-white needles; it is rapidly oxidised on exposure to air.

Diethylamidophenonaphthoxazine, $\text{NH}:\text{C}_{10}\text{H}_5\text{<}\overset{1}{\text{N}}\text{>}\overset{2}{\text{O}}\text{C}_6\text{H}_3\cdot\overset{4}{\text{NEt}_2}$, which

the authors refer to as "ethyl Nile blue," is prepared from nitroso-diethylmetamidophenol; it is obtained as the *hydrochloride*, which crystallises in lustrous, green needles, appearing blue by transmitted light; the salt is sparingly soluble in cold water, but dissolves readily in hot water, alcohol, and pyridine, yielding a blue solution. The *base* crystallises in green needles, which are brown by transmitted light; it is insoluble in water, but dissolves in common organic solvents, yielding fluorescent liquids. Reduction with zinc and hydrochloric acid gives rise to the *zincchloride* of the leuco-derivative, crystallising in white needles, which dissolve in water and are readily oxidised on exposure to air.

Tetramethylamidodiphenoxazinium chloride,



is obtained by adding nitrosodimethylmetamidophenol hydrochloride (20.2 grams) to a boiling solution of dimethylmetamidophenol (13.7 grams) in glacial acetic acid (150 grams); owing to its high degree of solubility in water, it is convenient to convert the chloride into the *iodide* by gradually adding hydrochloric acid in quantity sufficient to liberate the requisite amount of hydriodic acid from potassium iodide, and treating the boiling liquid with an aqueous solution of this salt. The iodide crystallises in blue needles having a green reflex, and contains $1\text{H}_2\text{O}$, which is removed in a vacuum; the solutions in water, acetone, and chloroform are blue, and exhibit strong brownish-red fluorescence.

Tetramethylamidodiphenoxazinium iodide is prepared from nitroso-diethylmetamidophenol hydrochloride by treating the *chloride* in the manner described; it crystallises from alcohol in blue needles having a vivid green reflex. The solutions of the iodide resemble those of the foregoing methyl derivative.

Dimethylamidophenonaphthoxazine, $\text{O}:\text{C}_{10}\text{H}_5\text{<}\overset{1}{\text{N}}\text{>}\overset{2}{\text{O}}\text{C}_6\text{H}_3\cdot\overset{4}{\text{NMe}_2}$, is ob-

tained by adding nitrosodimethylmetamidophenol hydrochloride (40 grams) to a boiling solution of α -naphthol (20 grams) in glacial acetic acid (200 grams); it melts at 244° , and crystallises from hot pyridine in large, green, lustrous prisms, which appear brownish-red in transmitted light. The dye is insoluble in water, but dissolves in common organic solvents, forming cherry-red solutions which exhibit scarlet fluorescence; the solutions in petroleum and benzene are yellowish-red, and exhibit green fluorescence. The *hydrochloride* crystallises in blue needles.

Diethylamidophenonaphthoxazine melts at 205° , and crystallises

from hot pyridine in prisms which appear brownish-red by transmitted, green by reflected, light; the solutions of the dye in organic solvents resemble those of the foregoing methyl derivative. It dissolves in concentrated sulphuric acid with a reddish-brown coloration, which becomes blue on dilution, and the solution in concentrated hydrochloric acid is yellowish-brown, and yields a blue precipitate when diluted with water.

The absorption spectra of the foregoing dyes have been examined, and are collected in a diagram which appears in the original paper.

M. O. F.

Action of Hypochlorous acid on Diazo-compounds. By THEODOR ZINCKE (*Ber.*, 1895, **28**, 2948—2951).—Paradiazobenzenesulphonic acid can be oxidised with a solution of bleaching powder, the solutions being kept cool with ice, to an acid, $\text{SO}_3\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\text{O}_3\text{H}$; evidence of the formation of intermediate products was obtained. The acid crystallises in reddish-yellow needles, which explode feebly when heated; the sodium, with H_2O , barium, and silver salts are respectively brownish-red, yellowish-white, and brownish-yellow. The acid possibly has the constitution, $\text{SO}_3\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{N}(\text{OH})\cdot\text{NO}_2$, but it is reduced by stannous chloride to Nietzki and Lerch's diamidobenzenesulphonic acid (*Abstr.*, 1889, 144).

C. F. B.

New Base from Isobutylidenephénylhydrazine. By KARL BRUNNER (*Monatsh.*, 1895, **16**, 849—865).—Whilst investigating the action of alcoholic zinc chloride on isobutylidenephénylhydrazine (compare *Abstr.*, 1895, i, 475), the author has isolated a new base by means of its compound with zinc chloride $(\text{C}_{10}\text{H}_{11}\text{N})_2\cdot\text{ZnCl}_2 + \frac{1}{2}\text{EtHO}$. This crystallises in pale yellow, hexagonal plates, melts at $170\text{--}172^\circ$, dissolves readily in benzene, alcohol, and ether, and may be reprecipitated by the addition of light petroleum; it is decomposed by water, and, when heated, yields dimethylindole. The free base, $(\text{C}_{10}\text{H}_{11}\text{N})_3$, is obtained by the addition of potassium hydroxide to a solution of the above-described compound with zinc chloride, and subsequent extraction with ether and recrystallisation from hot benzene. It dissolves in all ordinary organic solvents, and in mineral acids, and melts at $215\text{--}216^\circ$. The *picrate*, $\text{C}_{10}\text{H}_{11}\text{N}\cdot\text{C}_6\text{H}_3\text{N}_3\text{O}_7$, is sparingly soluble in ether, but dissolves readily in alcohol and benzene, crystallises in rhombic scales, and melts at $134\text{--}135.5^\circ$. The *bromo-derivative*, $\text{C}_{10}\text{H}_9\text{ONBr}_2$, melts at $180\text{--}181^\circ$.

By the action of sodium amalgam on the base, another base of the formula $\text{C}_{10}\text{H}_{13}\text{N}$ or $\text{C}_{10}\text{H}_{11}\text{N}$ is obtained; this crystallises in long needles, melts at 79° , and forms a platinochloride, which melts and decomposes at 205° .

G. T. M.

Preparation of Ketones from Aromatic Propenyl ($\text{CH}:\text{CHMe}$) Derivatives. By CARL HELL (*Ber.*, 1895, **28**, 2835—2838).—The compounds previously obtained from sodium ethoxide and isoeugenol ethyl and methyl ether dibromides (*Abstr.*, 1895, i, 657) are not alcohols, $\text{OH}\cdot\text{CR}\cdot\text{CHMe}$ or $\text{CHR}\cdot\text{CMe}\cdot\text{OH}$, but ketones, $\text{R}\cdot\text{CO}\cdot\text{CH}_2\text{Me}$, as they readily yield *phenylhydrazones*; that from the *ethyl* ether melts

at 86—87°, whilst the *methyl* derivative melts at 102—103°. By the action of bromine on the ketones, monobromoketones are formed. Anethoil dibromide and bromanethoil dibromide, by the action of chromic anhydride and glacial acetic acid, yield bromo-ketones, which are also formed when the products of the interaction of sodium ethoxide, anethoil dibromide, and bromanethoil dibromide respectively are brominated; these compounds are therefore α -ketones. The conversion of an aromatic propenylic dibromide into an α -ketone by means of sodium ethoxide takes place in four stages:

- (1) $R \cdot CHBr \cdot CHBrMe = R \cdot CBr : CHMe + HBr$,
- (2) $R \cdot CBr : CHMe + NaOEt = R \cdot C(OEt) : CHMe + NaBr$,
- (3) $R \cdot C(OEt) : CHMe + H_2O = R \cdot C(OH) : CHMe + EtOH$,
- (4) $R \cdot C(OH) : CHMe = R \cdot CO \cdot CH_2Me$. J. B. T.

Etherification of Aromatic Acids. By VICTOR MEYER (*Ber.*, 1895, **28**, 2773—2775).—In examining the constitution of aromatic acids by the etherification method, it is impossible to carry out the process in all cases at a low temperature, because some acids, which are only slightly soluble in alcoholic hydrogen chloride, do not undergo the reaction under these conditions. Moreover, the method of etherification by means of a current of hydrogen chloride passed into a boiling alcoholic solution cannot be generally used, because the characteristic differences in the behaviour of acids are often not shown when this process is employed. All simple acids, which do not contain more than two phenyl groups, behave in the characteristic way when they are boiled for 3—5 hours with alcohol containing 3 per cent. of hydrogen chloride (Fischer's method). More complex acids must be treated in solution in boiling alcohol with a current of hydrogen chloride. Several of the methyl derivatives of benzoic acid appear to behave in an exceptional manner, which is at present undergoing investigation. A. H.

Diamidobenzoic acids. By CARL HÄUSERMANN and H. TEICHMANN (*J. pr. Chem.*, 1895, [2], **52**, 428—429; compare *Abstr.*, 1895, i, 531).—*Ethyl*-2 : 5-diamidobenzoate is prepared from ethyl 2 : 5-dinitrobenzoate in the manner already described (*loc. cit.*). It is a yellowish powder, melts at 50·5—51°, and dissolves somewhat easily in hot water, and very easily in alcohol and benzene. In dilute ethereal solution, it has a greenish fluorescence.

The *hydrochloride*, $C_6H_3(NH_2)_2 \cdot COOEt, 2HCl$, and *sulphate* are described. A. G. B.

Products of the Reduction of Phenylbutyrolactone and Phenylparaconic acid. By RUDOLPH FITTIG, ADOLF WOLFF, and JOHN SHIELDS (*Annalen*, 1895, **288**, 203—209).—When phenylbutyrolactone is reduced with hydriodic acid, phenylbutyric acid is formed; this substance melts at 51·7°, and not at 47·5°, as stated by Jayne. The calcium salt contains $3H_2O$, and crystallises from water in long needles; it undergoes no change at 120°. Sodium amalgam has but

a slight action on a hot acid solution of phenylbutyrolactone; acetic acid and zinc dust give rise to a small proportion of phenylbutyric acid, 85 per cent. of the lactone employed being recovered unchanged. Tin and hydrochloric acid give rise to phenylbutyric acid, which is, for the most part, converted into the ethylic salt, the reaction being studied in alcoholic solution; 37 per cent. of the lactone remains unaltered.

Hydriodic acid converts phenylparaconic acid into benzylsuccinic acid, phenylbutyric acid being also formed as a secondary product.

M. O. F.

Action of Sodium Ethoxide on Phenylbutyrolactone.

By RUDOLPH FITTIG, ADOLF WOLFF, and RUDOLPH LESSER (*Annalen*, 1895, 288, 192—202; compare *Abstr.*, 1892, 813).—*Diphenyldibutyrolactone*.

$\text{CH}_2\text{CH}_2\text{CHPh}\cdot\text{O} \cdot \text{C} \cdot \text{C} \begin{smallmatrix} \text{CO} \cdot \text{O} \\ \text{CH}_2\text{CHPh} \end{smallmatrix}$, is obtained by heating phenylbutyrolactone with sodium ethoxide and alcohol for 15—18 hours in a reflux apparatus; it crystallises from alcohol in rosettes of colourless needles, and melts at 83—84°. The substance is unsaturated, and gives rise to three distinct compounds on treatment with bromine in carbon bisulphide solution; they melt at 109°, 150—151°, and 117—118° respectively.

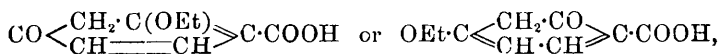
Diphenyloxetonecarboxylic acid, $\text{C}_{20}\text{H}_{20}\text{O}_4$, is obtained by heating the dilactone with aqueous sodium hydroxide and some alcohol; it decomposes at 147—148°. The *barium* salt decomposes above 100°, the *calcium* salt is anhydrous, and the *silver* salt becomes only slightly coloured on exposure to light.

Diphenyloxetone, $\text{C}_{18}\text{H}_{20}\text{O}_2$, is produced on heating the foregoing acid with dilute hydrochloric acid in a reflux apparatus, and is also slowly formed when water alone is used; it is a neutral oil, which undergoes slight decomposition when heated. Diphenyloxetone dissolves readily in organic solvents, with the exception of petroleum, which precipitates it completely from the solution in benzene; it does not reduce an ammoniacal silver solution, and yields no solid derivative with sodium hydrogen sulphite.

M. O. F.

Action of Ethylic Iodide on Potassium β -Resorcybate.

By GEORG GREGOR (*Monatsh.*, 1895, 16, 881—892).—*Ethoxy- β -resorcylic acid*, $\text{C}_7\text{H}_5\text{O}_3 \cdot \text{OEt}$, is formed, together with several neutral substances, by the action of ethylic iodide on potassium β -resorcybate in alcoholic solution. It crystallises in white needles, melts at 154°, and is sparingly soluble in cold water, but dissolves more readily in hot water, alcohol, ether, and benzene. The *sodium* salt, $\text{C}_9\text{H}_5\text{NaO}_4 + \text{H}_2\text{O}$, crystallises in scales; the *barium* salt is anhydrous, and crystallises in small needles; the *silver* salt contains $10\text{H}_2\text{O}$; the *lead* salt, $(\text{C}_9\text{H}_5\text{O}_4)_2\text{Pb} + 8\text{H}_2\text{O}$, and other salts are also described. From the behaviour of the ethylic salt towards dilute potassium hydroxide solution, the author concludes that the formula is



being derived from the secondary tertiary form, and not from the bi-tertiary form of resorcinol. He also suggests that the acid formed by the action of ethylic iodide on potassium- β -resorcyate perhaps consists of two isomeric acids, which are not easily separated (compare Tiemann and Parrisius, *Abstr.*, 1881, 271). G. T. M.

Halogen Derivatives of the Sulphonamides. By J. H. KASTLE (*Amer. Chem. J.*, 1895, **17**, 704—708).—Dichlorobenzenesulphonamide is readily prepared by dissolving benzenesulphonamide in the smallest quantity of soda (1 : 10), a rapid current of chlorine is passed through the solution, and the first portion of precipitate, which contains much unchanged sulphonamide, is removed, the filtrate treated with chlorine, the crude product washed with hot water by decantation, dissolved in alcohol, and precipitated by the addition of water. It is extremely stable. When heated at about 170°, it is resolved into chlorine, nitrogen, hydrogen chloride, and benzenesulphonic chloride, the latter being produced in almost theoretical quantity. By the action of bromine water on parachlorobenzenesulphonamide in soda solution, a yellow crystalline *dibromide* is formed. J. B. T.

Formation of Indigo in Plants of the Order Indigofera. By C. J. VAN LOOKEREN and P. J. VAN DER VEEN (*Landw. Versuchs. Stat.*, 1895, **46**, 249—258).—See this vol., ii, 207.

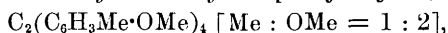
Coloured Aromatic Thioketones. By LUDWIG GATTERMANN (*Ber.*, 1895, **28**, 2869—2877).—*Paradiethoxythiobenzophenone*, $\text{CS}(\text{C}_6\text{H}_4\cdot\text{OMe})_2$, is prepared by the interaction of anisole, thio-carbonyl chloride, and aluminium chloride, and crystallises from alcohol in long, dark blue needles melting at 115°. Solutions of the ketone are of a bluish-violet colour; its constitution is shown by its conversion into dimethoxybenzophenone [$\text{CO} : \text{OMe} = 1 : 4$] when treated with alcoholic potash. Attempts to prepare derivatives of the thio-ketone were unsuccessful on account of the readiness with which the sulphur is eliminated.

Paradiethoxythiobenzophenone, $\text{CS}(\text{C}_6\text{H}_4\cdot\text{OEt})_2$, prepared in a similar manner from phenetole, crystallises in sky blue plates, melts at 118—119°, and, with alcoholic potash, is converted into paradiethoxybenzophenone. The molecular weight was determined by the cryoscopic method in naphthalene solution. *Paradipropoxythiobenzophenone*, $\text{CS}(\text{C}_6\text{H}_4\cdot\text{OPr}^a)_2$, from propoxybenzene, crystallises in blue plates and melts at 105—106°. *Paradipropoxybenzophenone*, $\text{CO}(\text{C}_6\text{H}_4\cdot\text{OPr}^a)_2$, formed by the action of alcoholic potash on the preceding compound, crystallises in colourless plates, and melts at 127°. The *oxime* is deposited in colourless needles melting at 113°. *Diethoxydimethylthiobenzophenone*, $\text{CS}(\text{C}_6\text{H}_3\text{Me}\cdot\text{OEt})_2$ [$\text{Me} : \text{OEt} = 1 : 2$], prepared from orthoethoxymethylbenzene, melts at 117—118°, and gives a violet solution in alcohol, from which it is deposited in olive-green needles with a steel-blue reflex; from light petroleum it crystallises in elongated steel-blue crystals. *Diethoxydimethylbenzophenone*, $\text{CO}(\text{C}_6\text{H}_3\text{Me}\cdot\text{OEt})_2$ [$\text{Me} : \text{OEt} = 1 : 2$], crystallises in

colourless, silky, lustrous needles melting at $105-106^{\circ}$. *Dimethoxydimethylthiobenzophenone*, $\text{CS}(\text{C}_6\text{H}_3\text{Me}\cdot\text{OMe})_2$ [$\text{Me} : \text{OMe} = 1 : 2$], could not be completely separated from the ketone, with which it appears to crystallise; the long, steel-blue needles obtained from its solution in light petroleum, dissolve with a violet coloration, and melt at 114° . *Dichlorodimethoxythiobenzophenone*, $\text{CS}(\text{C}_6\text{H}_3\text{Cl}\cdot\text{OMe})_2$ [$\text{Cl} : \text{OMe} = 1 : 2$], from orthochloranisole, crystallises in moss-green needles, melts at $178-179^{\circ}$, and dissolves with a violet colour. The ketone, $\text{CO}(\text{C}_6\text{H}_3\text{Cl}\cdot\text{OMe})_2$, crystallises in colourless needles, and melts at $183-184^{\circ}$. *Dichlorodiethoxythiobenzophenone*, $\text{CS}(\text{C}_6\text{H}_3\text{Cl}\cdot\text{OEt})_2$ [$\text{Cl} : \text{OEt} = 1 : 2$], crystallises in dark green needles, melts at $141-142^{\circ}$, and yields blue-violet solutions. The ketone, $\text{CO}(\text{C}_6\text{H}_3\text{Cl}\cdot\text{OEt})_2$, crystallises in colourless needles, and melts at $122-123^{\circ}$. *Dibromodimethoxythiobenzophenone*, $\text{CS}(\text{C}_6\text{H}_3\text{Br}\cdot\text{OMe})_2$ [$\text{Br} : \text{OMe} = 1 : 2$], from orthobromanisole, dissolves in alcohol with a violet colour, and crystallises with difficulty in dark green needles melting at $189-190^{\circ}$. The ketone, $\text{CO}(\text{C}_6\text{H}_3\text{Br}\cdot\text{OMe})_2$, crystallises in colourless needles melting at $180-181^{\circ}$.

The preceding thioketones, when heated at $200-220^{\circ}$ with finely divided copper, in an atmosphere of carbonic anhydride, yield cupric sulphide and derivatives of tetraphenylethylene. *Tetramethoxytetraphenylethylene*, $\text{C}_2(\text{C}_6\text{H}_4\cdot\text{OMe})_4$, from paradimethoxythiobenzophenone, crystallises from glacial acetic acid in colourless needles with a pale blue fluorescence, melts at $181-182^{\circ}$, and, in presence of bromine vapour or lead peroxide, yields a blue compound which has not yet been isolated. By the further action of lead peroxide at the ordinary temperature, the compound $\text{O} \begin{array}{c} \diagup \text{C}(\text{C}_6\text{H}_4\cdot\text{OMe})_2 \\ \diagdown \text{C}(\text{C}_6\text{H}_4\cdot\text{OMe})_2 \end{array}$, is obtained, it forms long,

colourless crystals melting at $188-189^{\circ}$. *Tetretethoxytetraphenylethylene*, $\text{C}_2(\text{C}_6\text{H}_4\cdot\text{OEt})_4$, resembles the methoxy-derivative, crystallises in long needles with an intense green fluorescence, melts at $120-121^{\circ}$, and, when reduced with sodium in alcoholic solution, yields *tetretethoxytetraphenylethane*, $\text{C}_2\text{H}_2(\text{C}_6\text{H}_4\cdot\text{OEt})_4$, which crystallises in colourless needles melting at $163-164^{\circ}$. *Tetrapropoxytetraphenylethylene*, $\text{C}_2(\text{C}_6\text{H}_4\cdot\text{OPr}^a)_4$, from dipropoxythiobenzophenone, crystallises in green, fluorescent needles, melts at $139-140^{\circ}$, and becomes blue when oxidised. *Tetramethoxytetramethyltetraphenylethylene*,



crystallises in fluorescent needles melting at 195° ; the corresponding ethoxy-derivative, $\text{C}_2(\text{C}_6\text{H}_3\text{Me}\cdot\text{OEt})_4$, is deposited from a mixture of pyridine and alcohol in green, fluorescent plates melting at 214° ; both compounds become blue when oxidised. *Tetrachlorotetramethoxytetraphenylethylene*, $\text{C}_2(\text{C}_6\text{H}_3\text{Cl}\cdot\text{OMe})_4$ [$\text{Cl} : \text{OMe} = 1 : 2$], crystallises from glacial acetic acid in colourless needles melting at 257° . The ethoxy-derivative, $\text{C}_2(\text{C}_6\text{H}_3\text{Cl}\cdot\text{OEt})_4$, is deposited from benzene in colourless, feathery crystals melting at $258-259^{\circ}$. Neither of these compounds becomes blue when oxidised. The compound, $\text{C}_2(\text{C}_6\text{H}_4\cdot\text{NMe}_2)_4$, is prepared by the action of copper on the corresponding thioketone and crystallises from acetone, on the addition of alcohol, in greenish-yellow needles, from benzene in highly lustrous prisms, melting at

310—315°. It is a strong base, which dissolves readily in dilute acids, and, on adding lead peroxide to its acetic acid solution, gives a dull, unstable violet coloration.

Bergreen prepared a reddish-brown oil by the interaction of benzene, thiocarbonyl chloride, and aluminium chloride; this experiment has been repeated, but a blue, oily liquid, consisting of a mixture of ketone and thioketone was obtained; these could not be separated. Other attempts to prepare thiobenzophenone by the action of hydrogen sulphide on benzophenoneanilide, to which a little hydrogen chloride had been added, and by the interaction of phosphorus pentasulphide in benzene solution, and benzophenone, were also unsuccessful; the latter method gave a product containing 50 per cent. of the thioketone, as shown by the production of tetraphenylethylene, which is not formed by heating copper with benzophenone. The colour of the above thioketones, and also that of thiacetophenone, shows that the group CS is a chromophore.

J. B. T.

Hydrazones of Fluorenone and its Derivatives. By GUIDO GOLDSCHMIEDT and FRANZ SCHRANZHOFFER (*Monatsh.*, 1895, **16**, 807—827).—The *phenylhydrazone* of fluorenone (diorthodiphenylene ketone) is obtained when an alcoholic solution of fluorenone is heated in a water bath with a slight excess of phenylhydrazine, and the product is subsequently acidified with acetic acid. On cooling, the compound separates in beautiful, yellow needles, and these, when recrystallised from alcohol form long prisms which melt at 151—151·5°.

When dry chlorine is led into a solution of the ketone in chloroform, the following two well characterised chlorinated derivatives are obtained:—*Chlorofluorenone* crystallises from dilute alcohol in long, yellow needles, melts at 115°, and forms a *phenylhydrazone* which melts at 139—141°. *β-Dichlorofluorenone* crystallises from alcohol in beautiful, long, yellow needles, melts at 188—189° (compare Hodgkinson and Matthews, *Trans.*, 1883, 165), and forms a *phenylhydrazone*,



which crystallises in yellow needles, and melts at 185—186°. *β-Dibromofluorenonephenylhydrazone* melts at 190°. *δ-Dibromofluorenone* melts at 262°, is yellow, and forms a *phenylhydrazone* melting at 252°. *Nitrofluorenonephenylhydrazone* melts at 210—214°. *α-Dinitrofluorenonephenylhydrazone* melts at 257—258°. *β-Dinitrofluorenone* forms yellow needles, melts at 220°, and yields a *phenylhydrazone* melting at 227—228°.

The results obtained in this investigation, taken in conjunction with the fact that ellagic acid, a fluorenone derivative, does not yield a hydrazone, have not thrown light on the formation of hydrazones, as expected by the authors.

G. T. M.

The Phthalein Groups. By RICHARD MEYER and HEINRICH MEYER (*Ber.*, 1895, **28**, 2959—2964).—Experiments undertaken to ascertain whether quinolphthalein, $\text{CO} < \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \text{O} \end{smallmatrix} > \text{C} < \begin{smallmatrix} \text{C}_6\text{H}_3(\text{OH}) \\ \text{C}_6\text{H}_3(\text{OH}) \end{smallmatrix} > \text{O}$, is related to fluoran, gave a negative result, and it was found impossible to decide

as to the structure of this substance. When it is heated with strong aqueous ammonia, it yields a colourless *imido-compound*, an imido-group having been substituted for one of the oxygen atoms; this compound decomposes above 310° without melting. The phthalein further yields a colourless *dibenzoate* melting at $252\text{--}253^{\circ}$. C. F. B.

Substitution Products of the Carbonates and Phosphates of α -Naphthol and β -Naphthol: Preparation of 1 : 4-Chloronaphthol and 1 : 4-Bromonaphthol. By FRÉDÉRIC REVERDIN and HUGO KAUFFMANN (*Ber.*, 1895, **28**, 3049—3058; compare *Abstr.*, 1895, i, 151).—4-Nitro- α -naphthyllic carbonate, $(\text{NO}_2\cdot\text{C}_{10}\text{H}_7\cdot\text{O})_2\text{CO}$, is obtained by the action of nitric acid on α -naphthyllic carbonate dissolved in glacial acetic acid; according to the quantity of the diluent employed, it is obtained in a form which crystallises from benzene in pale yellow needles melting at 148° , or as the modification separating in yellowish needles which melt at 212° . Both substances yield 1 : 4-nitronaphthol when hydrolysed with alcoholic potash, and in the case of the modification melting at 148° , α -naphthol is produced at the same time.

The *dichloride* of α -naphthyllic carbonate $(\text{C}_{10}\text{H}_7\text{Cl}_2\text{O})_2\text{CO}$, is formed when chlorine is led into a cold solution of α -naphthyllic carbonate in benzene or carbon tetrachloride; it crystallises in white needles, which melt and decompose at 200° . 4-Chloro- α -naphthyllic carbonate is produced when this substance is distilled or treated in chloroform solution with bases or acetic anhydride; it is also obtained by passing chlorine into a hot solution of α -naphthyllic carbonate in glacial acetic acid or a cold solution of this substance in carbon tetrachloride containing 5 per cent. of antimony trichloride. The compound is sparingly soluble in most solvents, and crystallises from benzene in white needles, which melt at 228° .

1 : 4-Chloronaphthol is obtained by hydrolysing chloro- α -naphthyllic carbonate with alcoholic potash; at 100° it sublimes in long, white needles, melting at 116° , and is readily soluble in organic solvents. A blue precipitate is formed when bleaching powder or ferric chloride is added to the neutral aqueous solution, and its behaviour in alkaline solution towards chloroform, carbon tetrachloride, and formaldehyde, resembles that of naphthol; it reacts with sodium nitrite and hydrochloric acid, and yields dyes with diazo-compounds. The *acetyl* derivative melts at 44° , and the *picrate* at 171° . 1 : 4-Chloronaphthol develops a blue coloration with dimethylparaphenylenediamine; 1 : 2 : 4-dichloronaphthol is produced when chlorine is passed into the solution in glacial acetic acid.

4-Bromo- α -naphthyllic carbonate crystallises from benzene and melts at 214° . When hydrolysed with alcoholic potash, it yields 1 : 4-bromonaphthol, which melts at $127\text{--}128^{\circ}$, and yields a *picrate* and an *acetyl* derivative which melt at 167° and 51° respectively; 1 : 4-bromonaphthol has also been obtained by the action of boiling water on diazotised 1 : 4-bromonaphthylamine, and when treated with bromine in glacial acetic acid solution it yields 1 : 2 : 4-dibromonaphthol, which melts at $105\cdot5^{\circ}$.

The behaviour of α -naphthyllic phosphate (m. p. $149\text{--}150^{\circ}$) closely resembles that of α -naphthyllic carbonate, and the substance yields a

sulphonic acid, the sodium salt of which, on hydrolysis, yields 1 : 4-naphtholsulphonic acid and sulphonaphthylphosphinate.

1-Bromo- β -naphthyllic carbonate is obtained by the action of phosgene on an alkaline solution of 1 : 2-bromonaphthol; it crystallises from ethylic acetate in white needles, and melts at 188—189°. 1-Iodo- β -naphthyllic carbonate crystallises in white needles, which become yellow on exposure to air, and melt at 188—189°.

M. O. F.

Paranthracene or Dianthracene. A Polymeric Modification of Anthracene. By WILLIAM R. ORNDORFF and F. K. CAMERON (*Amer. Chem. J.*, 1895, **17**, 658—681).—The paranthracene was prepared by the action of sunlight on anthracene suspended in benzene and xylene; the operation is expedited by shaking occasionally to remove deposited material from the glass. The product was purified by extraction with alcohol, ethylic acetate, and benzene, and the residue crystallised repeatedly from benzene in an extraction apparatus. Dimethylaniline is unsuitable as a solvent. Paranthracene crystallises in thin plates, which are fully described, belonging to the ortho-rhombic system $a : b : c = 0.6762 : 1 : 1.5731$; it melts at 242—244°, being quantitatively converted into anthracene; the same change takes place by prolonged heating alone at 230—235°, or in boiling naphthalene (218°), and partially in boiling dimethylaniline (192°), and in aniline (182°). The compound does not fluoresce either in solution or in the solid state. The sp. gr. = 1.265 at 27°/4°, and that of anthracene = 1.250; the following numbers express the solubility of paranthracene in the solvents (100 parts) at their respective boiling points: ethylenic bromide, 0.2273; pyridine, 1.106; anisole, 1.46; phenetole, 1.5. The molecular weight was determined by the boiling point method in the above solvents; the values are, in ethylenic bromide, 179—346, average of 10 determinations, 285; in pyridine, 317—387, average of 9 determinations, 354; in anisole, 331—397, average of 13 determinations, 362; in phenetole, 329—396, average of 8 determinations, 355. Elb's conclusion that the molecular weight of paranthracene is twice that of anthracene is thus confirmed, and it is suggested that this should be expressed by the name *dianthracene*.

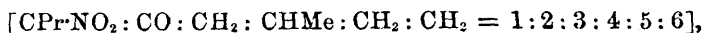
Attempts to prepare paranthracene by dropping a little of it into melted anthracene at 215—240°: by the action on it of hydrogen chloride, either aqueous or alcoholic, at 220°; by treatment of anthracene dibromide with zinc dust; by heating anthracene with sodium amalgam and alcohol, or with sodium and benzene, were all unsuccessful. Anthraquinone, dihydroanthracene, dichloranthracene, phenanthrene, retene, camphor, and phenylacridine were unchanged after exposure to light during several weeks; anthranol, in benzene solution, under these conditions, yielded an almost colourless product, which becomes brown and melts at 265—270°; it is insoluble in boiling alkali and less soluble in other media than anthranol. Acridine, in solution, when exposed to sunlight, gave a pale yellow, crystalline compound, which could not be dissolved, and which does not form salts with acids; when rapidly heated, it melts at 276°, when slowly heated it volatilises, without melting, at 250°, and, in both cases, is

converted into acridine; the same change is produced by prolonged boiling in various liquids. Graebe and Liebermann's formula is accepted for anthracene, with the modification that if von Baeyer's centric formula is adopted for benzene and its carboxylic acids, the benzene nuclei in anthracene must, from its synthetical formation, be represented in the same manner; the stability of anthraquinone and dihydroanthracene towards oxidising and reducing agents respectively is in accord with this. The difference in behaviour of anthracene and phenanthracene support the view that the former contains two benzene nuclei and two γ -carbon atoms (paraffinoid residue), and that the latter contains three benzene nuclei. With the above modifications, Linebarger's formula for paranthracene is accepted; its formation is ascribed to the tendency to form rings of six members, the para-linkage of the γ -carbon atoms being resolved. J. B. T.

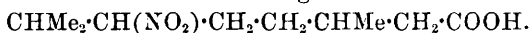
Limonene and its Derivatives. By EDWARD KREMERS (*Amer. Chem. J.*, 1895, **17**, 692—697).—The limonene employed boiled at 174.5 — 175° , and was prepared by the fractionation of commercial "carvene"; $[\alpha]_D = +120.466^\circ$, whilst the value given by Wallach and Conradi is 106.8° . The specific rotatory power of limonene solutions of varying content, in ordinary and absolute alcohol, chloroform, and glacial acetic acid, was determined; in the case of absolute alcohol and chloroform, the rotatory power decreases with fair regularity as the proportion of solvent rises. For solutions containing 10, 50, and 90 per cent. $[\alpha]_D = 113.430^\circ$ and 115.673° ; 115.690° and 117.604° ; 118.036° and 118.733° respectively. The fractions boiling at 172.5 — 177° have all a lower refractive power than limonene except the one boiling at 174 — 174.5° , for which $[\alpha]_D = 120.672^\circ$. Limonene hydrochloride, when treated with water in a sealed tube at the ordinary temperature, is slowly converted into terpene hydrate, which, when heated above its melting point, is resolved into terpene. When exposed to air, the oily mother liquid darkens, and the crystals gradually dissolve in it. J. B. T.

Nitration of Menthone. By MICHAEL I. KONOVALOFF (*Compt. rend.*, 1895, **121**, 652—653).—Nitric acid of sp. gr. 1.075 acts very readily on menthone, $C_{10}H_{18}O$, in sealed tubes at 100° , and yields nitromenthone, $NO_2 \cdot C_{10}H_{17}O$, a yellowish liquid with an odour recalling that of menthone. It boils and slightly decomposes at 135 — 140° under a pressure of 15 mm.; sp. gr. = 1.0856 at 0° and 1.0591 at 20° . It is insoluble in water, concentrated hydrochloric acid, and sodium carbonate solution, and only slightly soluble in concentrated aqueous potash. With sodium ethoxide in presence of alcohol, nitromenthone yields a salt which, when decomposed by sulphuric acid, gives a liquid acid of the composition $C_{10}H_{19}NO_4$. It boils and slightly decomposes at 190 — 195° under a pressure of 13 mm., and dissolves readily in sodium carbonate solution, but not in water or hydrochloric acid.

When reduced, nitromenthone yields a basic compound, and it seems to have the constitution



the constitution of the nitro-acid being



C. H. B.

Action of Silver Oxide on Dibromomenthylamine. Menthylhydrazine. By NIC. KIJNER (*J. pr. Chem.*, 1895, [2], **52**, 424—426).—*Menthonementhylhydrazone*, $\text{C}_{10}\text{H}_{19}\text{N}\cdot\text{N}\cdot\text{C}_{10}\text{H}_{18}$, is produced by adding moist silver oxide to dibromomenthylamine, warming at 50—60°, and extracting with ether. It crystallises in long, greenish-yellow needles, and melts at 92—93°. It is lævorotatory in solution ($[\alpha]_D = -366.5^\circ$). Boiling dilute hydrochloric acid converts it into menthone and *menthylhydrazine hydrochloride*, $\text{C}_{10}\text{H}_{19}\text{N}_2\text{H}_3\text{Cl}$, which dissolves in water, alcohol, and ether, and is lævorotatory ($[\alpha]_D = -46.05^\circ$). *Menthylhydrazine* is a liquid which boils at 235—240°, and by oxidation yields *menthane*, $\text{C}_{10}\text{H}_{20}$, which boils between 165—169°.

A. G. B.

Action of Hydroxylamine on l-Dibromomenthylamine. By NIC. KIJNER (*J. pr. Chem.*, 1895, [2], **52**, 426—427).—The author has published (*J. Russ. Chem. Soc.*, 1894, **26**, ii, 132) the result of the reaction between hydroxylamine hydrochloride and dibromomenthylamine. The change occurs in the sense of the equation $\text{C}_{10}\text{H}_{19}\cdot\text{NBr}_2 + \text{NH}_2\cdot\text{OH} = \text{C}_{10}\text{H}_{19}\text{Br} + \text{N}_2 + \text{H}_2\text{O} + \text{HBr}$.

It is pointed out that this reaction is analogous to that between hydroxylamine and dichloromethylamine, to which attention has just been called by Bamberger and Renauld (*Abstr.*, 1895, i, 494).

A. G. B.

Partial Synthesis of Camphor: Constitution of Camphoric acid and Camphorone. By JULIUS BREDT and M. VON ROSENBERG (*Annalen*, 1895, **289**, 1—14).—*Homocamphoric acid* is the name by which the authors refer to hydroxycamphocarboxylic acid, $\text{C}_{11}\text{H}_{18}\text{O}_4$, obtained by Haller (*Dissertation, Nancy*, 1879, 29) on hydrolysing cyanocamphor with aqueous caustic potash; the *silver salt* is a white powder dissolving with difficulty in water, and the calcium salt contains $7\text{H}_2\text{O}$, which is lost at 140°.

When the dry calcium salt of homocamphoric acid is distilled in an atmosphere of carbonic anhydride, camphor is produced in quantity amounting to 70 per cent. of the theoretical yield; camphor obtained in this way is in every respect identical with ordinary dextro-camphor.

The authors discuss the constitution of camphoric acid and camphorone.

M. O. F.

Tiemann's Formulæ for Camphor and Campholenic acid. By JULIUS BREDT (*Annalen*, 1895, **289**, 15—19).—The author draws attention to the identity of his expression for the constitution of camphor (*Abstr.*, 1894, i, 141) with the formula advocated by Tiemann (*Abstr.*, 1895, i, 426 and 675).

M. O. F.

Etherification and Hydrolysis. By JULIUS W. BRÜHL (*Ber.*, 1895, **28**, 2868—2869).—A question of priority with Wegscheider (this vol., i, 95) as to the discovery of the fact that, by the action of

hydrogen chloride and alcohol, the carboxyl group which is most readily etherified is subsequently also the most easily hydrolysed; this was shown three years ago by the author in the case of camphoric acid.

J. B. T.

Acids formed by Oxidation of inactive Campholenic acid.

By AUGUSTE BÉHAL (*Compt. rend.*, 1895, **121**, 465—468).—The acid, $C_6H_{10}O_4$, obtained by the action of nitric acid on inactive campholenic acid (this vol., i, 55) is identical with the unsymmetrical dimethylsuccinic acid, $COOH \cdot CMe_2 \cdot CH_2 \cdot COOH$, obtained by the interaction of ethylic bromisobutyrate and ethylic sodiomalonate. It melts at $143-144^\circ$; its anhydride melts at 22° , and yields with aniline an anilide melting at 185° , whilst the corresponding imide, obtained by the action of heat, melts at 86° .

It would seem to follow that the acid $C_7H_{12}O_4$ (*loc. cit.*) is a trimethylsuccinic acid or one of the dimethylglutaric acids, in which the two methyl groups are attached to the same carbon atom. The behaviour of hydroxycamphoronic acid on heating indicates that it probably has the constitution $COOH \cdot CMe_2 \cdot CH(CH_2 \cdot COOH)_2$.

C. H. B.

Synthesis of a New Ketonic acid. By E. BURKER (*Compt. rend.*, 1895, **121**, 607—610).—The action of camphoric anhydride on benzene in presence of aluminium chloride, if the temperature is not allowed to rise too high, yields an *acid* which, when purified, has the composition $C_{15}H_{16}O_2$, and forms small, nacreous, white crystals melting at $135-137^\circ$, and boiling at 320° under a pressure of 760 mm., or at 250° in a vacuum. Its molecular weight in solution in benzene is 232. It is almost insoluble in water, and very slightly in light petroleum, but dissolves readily in other organic solvents.

The alkali salts crystallise, and are decomposed by carbonic anhydride. The barium salt forms small, white, nacreous crystals containing $9H_2O$.

The *ethylic* salt, $C_{15}H_{18}O_2Et$, dissolves very readily in light petroleum, from which it separates in large monoclinic crystals. The *methyl* salt also crystallises from light petroleum in long monoclinic needles, which melt at $85-86^\circ$. Both are decomposed at once by sulphuric acid, but are very slowly attacked by alkalis. The *anhydride* is readily obtained by the action of acetic anhydride, but not by the action of acetic chloride; it forms small, white crystals which melt at about 135° , and are only slowly attacked by alcoholic potash. The *amide* forms long, silky, white needles which melt at 77° , and dissolve in boiling water; it is very slowly attacked by alcoholic potash. The *phenylhydrazide* forms long needles which melt at 156° .

The formation of this compound is readily explained by Friedel's formula for camphoric acid, but not by any formula which assumes the presence of two $COOH$ groups. Its constitution is therefore represented as $CHPr < \begin{smallmatrix} CH_2 \cdot CH_2 \\ CH_2 - CO \end{smallmatrix} > CPh \cdot OH$.

C. H. B.

Digitalin ("Digitalinum Verum"). By HEINRICH KILIANI (*Arch. Pharm.*, 1895, **233**, 698—699).—The author has succeeded in obtaining digitalin in a crystalline form by dissolving one part of the pure glucoside in two parts of boiling 85 per cent. methylic alcohol. The temperature of the solution is then allowed to fall gradually to 45°, at which point it is maintained; the substance is deposited in the form of white needles, in part aggregated to nodular masses. From a more dilute solution (1 in 10), the temperature of which is allowed to fall from the boiling point to the ordinary temperature, a small quantity of the substance is deposited wholly in the form of stellar aggregates of needles.

A. L.

Root of Aristolochia Argentina. By OSWALD HESSE (*Arch. Pharm.*, 1895, **233**, 664—697).—On account of its acid properties, the name *aristolochic acid* is suggested for Pohl's "aristolochine" (*Abstr.*, 1892, 874), the latter name being reserved for the alkaloid obtained from *Aristolochia argentina*. The author has obtained from the root of this plant a starch-like substance, a resin, an ethereal oil of high boiling point, palmitylphytosterin, $C_{42}H_{74}O_2$, aristolin, $C_{15}H_{28}O_3$, the isomeric aristic and aristidinic acids, $C_{18}H_{13}NO_7$, aristolic acid, $C_{15}H_{11}NO_7$ or $C_{15}H_{13}NO_7$, and the alkaloid aristolochine (compare *Abstr.*, 1892, 894).

The ethereal extract of the root is saturated with gaseous ammonia, and filtered from the resulting precipitate. The filtrate is neutralised, separated from ammonium and aristolochine salts, and evaporated. The residual, oily mass partially crystallises, the liquid portion on distillation yielding a colourless, highly refractive oil, having a disagreeable odour. Light petroleum separates the crystalline mass into soluble palmitylphytosterin and an insoluble substance—*aristolin*, $C_{15}H_{28}O_3$, probably an alcohol; it crystallises from alcohol in spherical aggregates of minute needles, and dissolves readily in ether and in hot alcohol. It melts and decomposes at 265°.

The precipitate produced by ammonia consists of a mixture of the ammonium salts of aristic, aristidinic, and aristolic acids, of which the first-named preponderates, and may be separated by means of its potassium salt, which is precipitated from solution on adding a slight excess of alkali. *Aristic acid*, $C_{18}H_{13}NO_7$, crystallises from acetic acid in greenish-yellow leaflets or needles which melt and decompose at about 275°, at higher temperatures evolving yellowish vapours which condense to form a yellow sublimate. When it is fused with potash, ammonia is evolved. It forms two series of salts, a normal and a basic; the former alone have been obtained in a crystalline form. The *potassium* salt, $C_{18}H_{12}NO_7K \cdot 2H_2O$, forms small red crystals, but when anhydrous is yellow. The *sodium* salt resembles that of potassium. The *ammonium* salt crystallises in red needles. The *barium*, $(C_{18}H_{12}NO_7)_2Ba \cdot 2H_2O$, *calcium*, $(C_{18}H_{12}NO_7)_2Ca \cdot 4H_2O$, *copper*, $(C_{18}H_{12}NO_7)_2Cu \cdot 3H_2O$, *lead*, $(C_{18}H_{12}NO_7)_2Pb \cdot 2H_2O$, and *silver* salts, $C_{18}H_{12}NO_7Ag$, crystallise in small, orange needles. The *methylic* salt, $C_{18}H_{12}NO_7Me$, forms yellow needles, and melts at about 250°.

The potassium salt of aristidinic acid is separated from that of aristolic acid by adding to the solution a large excess of potash, in which the former salt is insoluble. *Aristidinic acid*, $C_{18}H_{13}NO_7$, is soluble in acetic acid and in alcohol; it forms small, greenish-yellow crystals which darken at 230° , and melt at 260° . *Aristolic acid*, $C_{15}H_{11}NO_7$ or $C_{18}H_{13}NO_7$, is readily soluble in ether, acetic acid, and hot alcohol, and crystallises from the latter in small, orange-red needles, which darken at 223° , and melt at $260-270^\circ$. These three acids and aristolochic acid dissolve in warm sulphuric acid, forming beautiful dark green solutions; this appears to indicate that these substances are closely allied in constitution. It is possible that aristolochic acid is the next higher homologue of aristic acid, and that aristidinic acid is methylaristolochic acid. The latter view is supported by the circumstance that aristidinic acid appears to contain a methoxyl group. A. L.

Chlorophyll. By EDWARD SCHUNCK and LEO MARCHLEWSKI (*Annalen*, 1895, 288, 209—218; compare Abstr., 1894, i, 341, and 1895, i, 296).—The authors, having already established analytically the composition of phyllotaonin (*loc. cit.*), confirm the expression, $C_{40}H_{40}N_6O_6$, by ebullioscopic determinations of the molecular weight. Phyllotaonin is indifferent towards hydroxylamine, and has no reducing action on Fehling's solution or an ammoniacal solution of silver; this behaviour indicates that phyllotaonin and chlorophyll are not aldehydic in character. Owing to the opacity of dilute solutions containing ethylphyllotaonin, it is not possible to determine whether this substance is optically active; the authors consider, however, that this is probably the case, because phyllotaonin forms monosymmetric crystals which exhibit hemihedral faces.

When ethylphyllotaonin is distilled from zinc dust, a small quantity of an oil is produced which becomes brown on exposure to the atmosphere, and yields a red powder when treated with hot, dilute hydrochloric acid; moreover, the vapour which is evolved by phyllotaonin, when heated in a dry tube, produces an intense red stain on a fir splinter which has been moistened with hydrochloric acid. These facts are recognised as indicating relationship between chlorophyll and pyrroline; Nencki and Sieber have recorded a similar observation in connection with hæmatoporphyrin.

The remaining portion of the paper is devoted to criticism of Etard's investigation of lucern (Abstr., 1895, i, 389), the results of which the authors regard as erroneous. M. O. F.

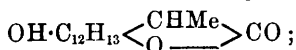
The Yellow Colouring Matter of Autumn Leaves. By GEORG STAATS (*Ber.*, 1895, 28, 2807—2809).—The yellow colouring matter which may be extracted from autumnal leaves by boiling alcohol is not identical with phyloxanthin, and is called by the author *autumnixanthin*. From whatever source the yellow colouring matter is derived, its alcoholic solution gives, with potash, a reddish-brown precipitate, which dissolves in water or acids. The potassium compound has been obtained in minute crystals, but has not been analysed. The autumnixanthine itself has not been obtained crystal-

line. When its alcoholic solution is slowly added to boiling hydrochloric acid, a red solution is formed. A. H.

Pelagëine. By ARTHUR B. GRIFFITHS and C. PLATT (*Compt. rend.*, 1895, **121**, 451—452).—The violet pigment of the medusa dissolves with the fats in alcohol and ether. The filtered solution is evaporated to dryness, treated with sodium hydroxide, and the pigment extracted with carbon bisulphide. It is an amorphous product of the composition $C_{20}H_{17}NO_7$, insoluble in water, soluble in alcohol, ether, and ethylic acetate, and very soluble in carbon bisulphide. The solutions show no characteristic absorption bands. When exposed to light, the pigment is decolorised. C. H. B.

The Four Santonous acids. By AMERICO ANDREOCCHI (*Gazzetta*, 1895, **25**, i, 452—568).—In alcoholic solution, santonin has the specific rotation $[\alpha]_D = -173$, the rotation increasing to -176.5 in 80 per cent. alcohol, whilst when dissolved in 38 per cent. hydrochloric acid or hydrobromic acid (sp. gr. 1.38), the value of $[\alpha]_D$ becomes -340 and -345 respectively, although the santonin is precipitated unchanged by addition of water; the increase in rotation is probably due to the conversion of the ketonic group into a $:C(OH)X$ group, by addition of water or of the halogen hydride. The behaviour of santonic acid is similar; in 100 and 50 per cent. alcohol it has the specific rotations $[\alpha]_D = -42.1$ and -74.1 respectively, and in 9.5 and 38 per cent. hydrochloric acid $[\alpha]_D = -87.9$ and -138.6 respectively.

Methyl-desmotroposantonin, $OMe \cdot C_{12}H_{13} < \underset{O}{\text{CHMe}} > CO$, is obtained together with methylis-desmotroposantonin, by the action of sodium methoxide and methylic iodide on desmotroposantonin,



it crystallises in long needles melting at $152-153^\circ$, has the specific rotation $[\alpha]_D = +91.9$ in absolute alcohol, and dissolves sparingly in the usual solvents. It behaves like an alkylated phenol and is but slowly converted by boiling alkalis into methyl-desmotroposantononic acid. The corresponding *ethyl* derivative, $C_{17}H_{22}O_3$, is similar in preparation and properties; it crystallises in long needles melting at 168° and has the specific rotation $[\alpha]_D = +114.0$ to 114.2 in absolute alcohol. The *benzyl* derivative also, prepared by the action of sodium ethoxide and benzylic chloride, crystallises in needles melting at 182° , and has the specific rotation $[\alpha]_D = +102.6$.

Isodesmotroposantonin crystallises in needles melting at $187-188^\circ$, and in absolute alcohol has the specific rotation $[\alpha]_D = +128.8$. It yields *methylis-desmotroposantonin*, $OMe \cdot C_{12}H_{13} < \underset{O}{\text{CHMe}} > CO$, on treatment with sodium methoxide and methylic iodide; this crystallises in needles melting at $111-112^\circ$, and in alcohol has $[\alpha]_D = +118.2$. The corresponding *ethyl* compound crystallises in hemimorphic, monoclinic prisms melting at 82° ; $a:b:c = 0.2718:1:0.2556$; $\beta = 80^\circ 20'$; it is very soluble in ether, chloroform, or alcohol, and

in the latter solution has the specific rotation, $[\alpha]_D = +129.6$. The corresponding *benzyl* derivative crystallises in small needles melting at 82° , and has $[\alpha]_D = +136.5$ in alcoholic solution.

Dextrosantonous acid (compare Cannizzaro and Cernelutti, Abstr., 1883, 77) melts at $179-180^\circ$ and distils unchanged at $200-260^\circ$ under 5 mm. pressure; it has the specific rotation, $[\alpha]_D = +74.9$ in alcoholic solution, and has the normal molecular weight in freezing acetic acid. If santonin is reduced with tin and boiling hydrochloric acid, less santonous acid is obtained, but *paradimethylethylclothydronaphthalene*, $C_{10}H_{13}Me_2Et$, is formed; when purified from an additive compound with hydrogen chloride by fractionation from sodium, it is a limpid colourless oil which boils at $247-248^\circ$ under ordinary pressure, and gives the normal vapour density by V. Meyer's method.

Methylic dextrosantonite (compare Cannizzaro and Cernelutti, *loc. cit.*), melts at 86° , and has the specific rotation $[\alpha]_D = +84.9$ in alcohol. The ethylic salt gives $[\alpha]_D = +71.0$ in alcohol, and the crystals phosphoresce when crushed, whilst the *benzoyl* derivative, $OBz \cdot C_{12}H_{11} \cdot CHMe \cdot COOEt$, melts at 75° and gives $[\alpha]_D = +59.9$.

Dextromethylsantonous acid, $OMe \cdot C_{12}H_{11} \cdot CHMe \cdot COOH$, is prepared by the action of sodium methoxide and methylic iodide on dextrosantonous acid or its ethylic salt; its *ethylic* salt crystallises in prisms melting at $116-117^\circ$, is soluble in alcohol, ether, light petroleum, or cold alkaline carbonates and has the specific rotation $[\alpha]_D = +72.2$, in alcoholic solution. Dextro-ethylsantonous acid melts at 120° , and its ethylic salt has the specific rotation $[\alpha]_D = +70.5$ in alcohol.

Ethylic dextrobromosantonite, $OH \cdot C_{14}H_{17}Br \cdot COOEt$, prepared by brominating ethylic dextrosantonite, forms beautiful hemihedral orthorhombic crystals melting at 86° , and is very soluble in ether, alcohol, or ethylic acetate; it has the specific rotation $[\alpha]_D = +68.2$ in alcohol. It is precipitated unchanged from its solution in potash by carbonic anhydride, but if the solution is heated or kept, a mixture of two isomeric dextrobromosantonous acids is obtained. *α -Dextrobromosantonous acid*, $C_{15}H_{19}BrO_3$, is very soluble in ether, from which it crystallises, with $\frac{1}{2}Et_2O$, in tablets which melt for the first time at 110° , and after solidification at $115-116^\circ$; the pure acid has the specific rotation $[\alpha]_D = +69.7$ in alcohol. *β -Dextrobromosantonous acid*, is sparingly soluble in ether, crystallises in pyramids melting at $159-160^\circ$, and has the specific rotation $[\alpha]_D = +61.9$. On treatment with alcohol and hydrogen chloride, the α -acid yields the ethylic salt from which it is prepared, whilst the β -isomeride gives a viscous uncrystallisable mass.

No crystalline products were obtained on oxidising dextrosantonous acid with permanganate, ferricyanide, or chromic acid, and on boiling the acid with iodine in acetic acid solution, a green amorphous *substance* having the composition of a dimethylnaphthaquinonepropionic acid, $C_{15}H_{14}O_4$, was formed; this dissolves in water, alcohol, and alkalis giving fluorescent solutions. On boiling dextrosantonous acid with dilute acetic acid and ferric chloride, *dextrodisantonous acid*, $COOH \cdot CHMe \cdot C_{12}H_{13}(OH) \cdot C_{12}H_{13}(OH) \cdot CHMe \cdot COOH$, is formed; it crystallises in small needles melting at $250-250.5^\circ$, is soluble in

alcohol, acetic acid, or alkali carbonates, and has the specific rotation, $[\alpha]_D = +89.5$ in alcohol, and the normal molecular weight in freezing acetic acid. Its *diethylic* salt, prepared by means of alcohol and hydrogen chloride, crystallises in colourless prisms melting at 183° , and depresses the freezing point of benzene normally. The two *methyllic* salts melt at 158° and 215° , but were not analysed.

A comparison of the rotatory powers of the *lævosantonous* acid, prepared by reducing isodesmotroposantonin (Abstr., 1894, i, 205) with those of its dextro-isomeride, shows that the two substances are enantiomorphous; when crystallised together they yield the inactive isosantonous acid melting at 153 — 155° .

Methyllic lævosantonite crystallises in large prisms melting at 86° , and is very soluble in alcohol, ether, or light petroleum. The *ethylic* salt crystallises in large, hemimorphic, monoclinic prisms which melt at 116 — 117° and become phosphorescent when crushed; $a:b:c = 0.5628:1.06959$; the specific rotation in alcohol is $[\alpha]_D = -70.4$. *Ethylic lævobenzoylsantonite* crystallises in long needles melting at 75° , and has the specific rotation $[\alpha]_D = -59.8$ in alcohol, that of its dextro-isomeride being $+59.9$. *Ethylic lævoscdiosantonite* behaves just like the dextro-compound.

Lævomethylsantonous acid, $\text{OMe} \cdot \text{C}_{12}\text{H}_{14} \cdot \text{CHMe} \cdot \text{COOH}$, is prepared by the action of sodium methoxide and methyllic iodide on *lævosantonous acid*, or by reducing methylisodesmotroposantonin with zinc dust and acetic acid; it crystallises in pyramids melting at 116 — 117° , and is very soluble in ether. *Ethylic lævo-ethylsantonite* also prepared from *lævosantonous acid*, crystallises in needles melting at 31 — 32° , and has the specific rotation $[\alpha]_D = -70.3$; the *acid* crystallises in colourless needles melting at 120° , and has the specific rotation $[\alpha]_D = -73.1$. *Lævobenzylsantonous acid* is obtained as a gum. On brominating *ethylic lævosantonite* in carbon tetrachloride solution, *ethylic lævobromosantonite* is obtained in large, hemihedral, orthorhombic crystals, which melt at 86° , and are enantiomorphous with those of the dextro-isomeride; $a:b:c = 0.5317:1.10649$; it has the specific rotation $[\alpha]_D = -68.5$, and on hydrolysis yields *lævo- α -bromosantonous acid*, which crystallises with $\frac{1}{2}\text{Et}_2\text{O}$, melts at 110 — 111° and 115 — 116° like its dextro-isomeride, and has the specific rotation $[\alpha]_D = -69.4$. *Lævodisantonous acid* crystallises in needles melting at 250 — 250.5° , and has the specific rotation $[\alpha]_D = -85.8$. The behaviour and properties of these *lævorotatory* substances are very similar to those of their dextro-isomerides.

The isosantonous acid of Cannizzaro and Carnelutti (*loc. cit.*) is identical with the racemic santonous acid obtained by crystallising equal weights of dextro- and *lævo*-santonous acid together, and melts at 153° . The *methyllic* salt melts at 110.5 — 111° . Racemic *ethylic santonite* crystallises in small, colourless, anorthic crystals which melt at 125° , and do not become phosphorescent like those of its active isomerides when crushed; $a:b:c = 1.6891:1.07930$; $\alpha = 92^\circ 59'$, $\beta = 112^\circ 3'$, $\gamma = 85^\circ 25'$; cryoscopic determinations show it to be dissociated into its components in acetic acid solution. Racemic *ethylic benzoylsantonite* melts at 89° .

Racemic methylsantonous acid crystallises in small prisms melting

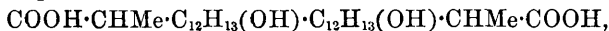
at 135—135·5°, and the corresponding ethyl compound melts at 144—145°, not at 143°, as previously stated; *racemic ethylic bromosantonite*, $\text{OH}\cdot\text{C}_{12}\text{H}_{13}\cdot\text{Br}\cdot\text{CHMe}\cdot\text{COOEt}$, melts at 104—106°, and on hydrolysis yields *racemic α -bromosantonous acid* which melts at 193—195°. *Inactive disantonous acid* crystallises in small pyramids melting at 243—244°.

Methyldesmotroposantonous acid melts at 107—108° and has the specific rotation $[\alpha]_D = -48\cdot9$; the corresponding *ethyl* compound, $\text{OEt}\cdot\text{C}_{12}\text{H}_{13}\cdot\text{CHMe}\cdot\text{COOH}$, crystallises in large, anorthic prisms melting at 127°, and has the specific rotation $[\alpha]_D = -47\cdot2$ in alcoholic solution; $a:b:c = 1\cdot1269 : 1 : 0\cdot6013$; $\alpha = 69^\circ 40'$, $\beta = 130^\circ 47'$, $\gamma = 119^\circ 52'$. The *ethyl* salts of both these acids are viscous liquids.

*Benzyl*desmotroposantonous acid, $\text{C}_7\text{H}_7\text{O}\cdot\text{C}_{12}\text{H}_{13}\cdot\text{CHMe}\cdot\text{COOH}$, prepared by reducing benzyl-desmotroposantonin with zinc dust and acetic acid, crystallises in prisms melting at 120—121°, and has the specific rotation $[\alpha]_D = -39\cdot3$ in alcohol.

Methylic desmotroposantonite (Abstr., 1894, i, 205) has the specific rotation $[\alpha]_D = -41\cdot8$ in alcoholic solution; the *sodium* derivative of this and the corresponding *ethyl* salt are white powders. *Methylic bromodesmotroposantonite*, $\text{OH}\cdot\text{C}_{12}\text{H}_{13}\cdot\text{Br}\cdot\text{CHBr}\cdot\text{COOMe}$, prepared by direct bromination, is a syrupy liquid which when hydrolysed with potash yields *bromodesmotroposantonous acid*; it crystallises with ether or petroleum, in needles melting at 92°, and has the specific rotation $[\alpha]_D = -50\cdot4$ in alcohol.

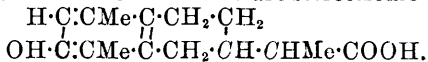
Desmotropodisantonous acid,



is prepared by oxidising desmotroposantonous acid with ferric chloride; it crystallises in laminæ melting at 254—255°, and has the specific rotation $[\alpha]_D = -64\cdot5$ in alcohol.

On heating desmotroposantonous acid at 295—305°, a resinous anhydride is obtained which, when precipitated from its sodium carbonate solution by hydrochloric acid, yields *lævosantonous acid*. When fused with potash, each of the four santonous acids breaks up quantitatively yielding hydrogen, propionic acid, and the same *para*-dimethyl- β -naphthol (compare Cannizzaro and Carnelutti, *Gazzetta*, 13, 385); it crystallises in lustrous needles melting at 135—136°, and boils at 315—316° under 760 mm. pressure; its methyl derivative crystallises in prisms melting at 68°. The same *dimethyl-naphthol* is obtained, together with propionic acid and hydrogen bromide on fusing *dextro- α -bromosantonous acid* with potash; if the mixture is fused for only a short time, an ill-defined *acid*, which probably has the constitution $\text{OH}\cdot\text{C}_{12}\text{H}_{12}\cdot\text{CHMe}\cdot\text{COOH}$, is obtained.

The author concludes that the four santonous acids are stereoisomerides having the constitution



The two carbon atoms indicated by italics are asymmetric and of different kinds; therefore four optically active and two racemic santonous acids should exist. Representing the asymmetric carbon atom of greatest optical activity by *A*, and that of lesser by *B*, *dextro-*

and lævosantonous acids should contain $+A + B$ and $-A - B$ respectively, whilst desmotroposantonous acid should contain $-A + B$; the racemic santonous acid should be compounded of $+A + B$ and $-A - B$.

W. J. P.

Pyridine Periodides. By ALBERT B. PRESCOTT and P. F. TROWBRIDGE (*J. Amer. Chem. Soc.*, 1895, **17**, 859—869).—*Pyridine methyl pentiodide*, $C_5NH_5MeI_5$, is obtained by adding an alcoholic solution of pyridine methiodide to a solution of the requisite quantity of iodine in alcohol. After recrystallisation from alcohol, it forms long, greenish-black needles, and melts at 47.5° .

Pyridine methyl diiodide forms reddish-brown needles and melts at 91.5° . The crystals are very stable; after eight months, no appreciable decomposition was observable. The *triiodide* forms fine, dark red needles, is perfectly stable, and melts at 50° . *Dipyridine dimethyl enneaiodide*, $(C_5NH_5CH_3I)_2I_9$, crystallises in greenish-black, lustrous needles, and melts at 44° . The *octaiodide* is still under investigation.

Pyridine ethyl triiodide melts at 49° . *Pyridine tetraiodide*, obtained by adding to pyridine an alcoholic solution of iodine until a precipitate ceased to form, crystallises in fine, dark green, lustrous needles; it is readily soluble in alcohol, ether, and chloroform, less readily in benzene, melts at 85° , and is less stable than the compounds previously described.

The authors have also prepared Dafert's pyridine hydrogen pentiodide (Abstr., 1883, 980); the analyses agree with the formula $C_5NH_5HI_5$. The melting point is given as 85° (Dafert gives 89°). The paper concludes by giving instructions for the estimation of iodine in periodides.

J. J. S.

The Pyridine Series. By ARTHUR PHILIPS (*Annalen*, 1895, **288**, 253—265; compare Abstr., 1893, i, 727, and 1894, i, 301).—The main facts recorded in this paper have been already described (*loc. cit.*).

M. O. F.

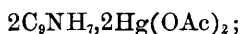
Mercuroquinoline Compounds. By LEONE PESCI (*Gazzetta*, 1895, **25**, i, 394—406).—*Quinoline mercuric chloride*, $2C_9NH_7HgCl_2$, is prepared by mixing alcoholic solutions of quinoline and mercuric chloride; it crystallises in colourless, thin needles or small rhombohedra, decomposes at 150 — 200° , and is insoluble in cold water. On mixing the proper proportions of quinoline and mercuric chloride in alcoholic solution, a salt of the composition $2C_9NH_7, 2HgCl_2$ may be obtained; it crystallises in microscopic prisms and is soluble in boiling alcohol. On heating the first salt described above with quinoline hydrochloride in aqueous solution, a salt of the composition $11C_9NH_7, 5HgCl_2, HCl$ is obtained; it crystallises in colourless, transparent, anorthic prisms melting at 143° , and is soluble in boiling alcohol. A salt of the composition $7C_9NH_7, 3HgCl_2, HCl$, which crystallises in thin, colourless needles, was also prepared.

A compound of the composition $2C_9NH_7, HgCl_2, PtCl_4$ is deposited as a yellow, amorphous powder on mixing solutions of quinoline

mercuric acetate and hydrogen platinochloride; it melts and decomposes at 140—141°.

Quinoline mercuric nitrate, $2C_9NH_7, Hg(NO_3)_2, 2H_2O$, prepared by treating the corresponding acetate with potassium nitrate, crystallises in colourless, transparent prisms, melting and decomposing at 183—184°. *Quinoline mercuric sulphate*, $2C_9NH_7, HgSO_4$, separates in colourless octahedra on adding quinoline to mercuric sulphate solution; it melts and decomposes at 140—142°.

Quinoline mercuric acetate, $2C_9NH_7, Hg(OAc)_2, 2H_2O$, separates in large, transparent, orthorhombic crystals on cooling a solution of quinoline in mercuric acetate solution; it is soluble in chloroform, benzene, or water, and is most soluble in water at 40°, for above this temperature the solution becomes turbid and deposits an oily substance. It melts at 148°, and is decomposed by boiling water, giving mercuric oxide, quinoline, and a salt of the composition



the latter crystallises in colourless needles melting at 156°, and may be also prepared by mixing quinoline and mercuric acetate solution in the proper proportion. *Quinoline mercuric oxalate*, $2C_9NH_7, HgC_2O_4$, prepared by the interaction of the corresponding acetate and potassium oxalate, crystallises in colourless laminæ, melting and decomposing at 177—178°.

The above compounds may be regarded as salts of *quinoline mercuric hydroxide*, $2C_9NH_7, Hg(OH)_2$, a solution of which can be readily prepared by treating the corresponding sulphate with barium carbonate; the solution is colourless, and has a strongly alkaline reaction towards litmus, but is indifferent towards phenolphthaleïn. The pure base could not be isolated, for, on evaporating the solution, quinoline and mercuric oxide separate; the base in solution reacts quantitatively with sodium thiosulphate, yielding quinoline, mercuric thiosulphate, and caustic soda; with potassium iodide, giving quinoline, mercuric iodide, and caustic potash; and with ammonium bromide, giving quinoline, mercuric bromide, and ammonia.

W. J. P.

Synthesis of Quinoline Derivatives from Anthranilic acid and Aldehydes. By STEFAN NIEMENTOWSKI and B. ORZECOWSKI (*Ber.*, 1895, **28**, 2809—2822; compare *Abstr.*, 1894, i, 427).—Acetaldehyde reacts readily with anthranilic acid to form *ethylideneanthranilic acid*, $COOH \cdot C_6H_4 \cdot N \cdot CHMe$, which, however, could not be obtained quite pure, as it partially decomposes when recrystallised. *Trichlorethylideneanthranilic acid* is obtained from chloral and anthranilic acid; it crystallises in rhombic tablets, melts at 152°, and is decomposed by boiling water into anthranilic acid and chloroform. *Propylideneanthranilic acid* is a yellow powder which melts at 115°. When this compound or its constituents are heated on the water bath, *3'-methyl-2'-ethylquinoline-1-carboxylic acid* is formed; it crystallises in pale yellow needles or plates, melting at 221°. This substance is accompanied by *methyl ethylacroleinanthranilic acid*,



which is a yellow, amorphous mass, and is converted into the foregoing substance when its alcoholic solution is preserved. The carboxylic acid, on distillation, yields the 3'-methyl-2'-ethylquinoline described by Doebner and Miller (Abstr., 1884, 1376). This is accompanied by other products, which have not yet been examined.

Oenanthaldehyde reacts with anthranilic acid at the ordinary temperature to form a polymeric *heptylideneanthranilic acid*, $C_{28}H_{38}N_2O_4$, which melts at 183° , and is converted into the compound, $C_{14}H_{16}NO_2$, when it is heated for some time at its melting point; the latter crystallises well and melts at 93° . When it is heated with a strong acid or an alkali, it is converted into 3'-amyl-2'-hexylquinoline-1-carboxylic acid, which crystallises in rhombic tablets melting at 69° . The *hydrochloride* is formed when hydrogen chloride is passed into an ethereal solution of heptylideneanthranilic acid. The carboxylic acid may also be obtained by heating heptylideneanthranilic acid with acetic anhydride. Oxygen is absorbed from the air and acetanthranilic acid formed. On distillation, the acid yields 3'-amyl-2'-hexylquinoline. 4'-Hydroxy-3'-amylquinoline is formed in small amount when heptylideneanthranilic acid is heated at 200° in a sealed tube, and forms broad, silky needles, melting at 85° .

The author has also obtained a substance of the formula $C_{21}H_{26}N_2O_2$ by the condensation of oenanthaldehyde and anthranilic acid under conditions which have not been precisely defined. It crystallises in yellow needles melting at 243° .
A. H.

Compounds of Antipyrine (Dimethylphenylpyrazolone) with Dihydric Phenols. By GUSTAVE PATEIN and E. DUFAU (*Compt. rend.*, 1895, 121, 532—534).—*Catecholdiantipyrine* is obtained by mixing aqueous solutions of its constituents; it forms colourless crystals, which melt at 78 — 79° , and are very soluble in alcohol and chloroform, slightly soluble in ether or water. With ferric chloride solution, a greenish-black coloration is produced. Guaiacol or methylcatechol combines with only one molecular proportion of antipyrine, and veratrol or dimethylcatechol does not combine with it at all. Resorcinol combines with only one molecular proportion of antipyrine, and the product, which melts at 103 — 104° , gives a blood-red coloration with ferric chloride.

Quinol, like catechol, combines with two molecular proportions of antipyrine, and the product crystallises in colourless needles, which melt at 127 — 128° and are very soluble in boiling water or alcohol, slightly soluble in ether, and soluble in, but decomposed by, chloroform. With ferric chloride, a deep red coloration is produced, changing, after a time, to pale red. In presence of the slightest excess of quinol, decolorisation is instantaneous, and quinhydrone is precipitated.

These products cannot be regarded as mere molecular combinations, and it is probable that combination takes place between the hydroxyl groups and the nitrogen which is in connection with the methyl group in the antipyrine, this nitrogen becoming quinquivalent.

It is noteworthy that the ortho- and para-dihydric phenols combine with 2 mols. of antipyrine, whereas the metadihydric phenol combines only with one, and this power of combination disappears in

proportion as the hydroxyl groups are displaced by a metal or an alkyl radicle. C. H. B.

Diphenylisoxazole. By CARL GOLDSCHMIDT (*Ber.*, 1895, 28, 2540).—Benzylideneacetophenone dissolved in ether is converted by chlorine into *benzylideneacetophenone* $\alpha\beta$ -dichloride,



which melts at 113°. This substance reacts with hydroxylamine to form *diphenylisoxazole*, $\text{N} \begin{smallmatrix} \text{CPh}\cdot\text{CH} \\ \text{O} \end{smallmatrix}$, which crystallises in nacreous plates, melting at 141°.

This compound and phenylmethylisoxazole are converted by alcoholic ammonia at 250° into crystalline bases, an account of which will shortly be published. A. H.

Action of Hydroxylamine on Ethylic Benzylideneacetoacetate. By EMIL KNOEVENAGEL and W. RENNER (*Ber.*, 1895, 28, 2994—3000; compare R. Schiff, this vol, i, 83).—Hydroxylamine hydrochloride in alcoholic solution reacts with ethylic benzylideneacetoacetate when warmed for some 30 minutes on the water bath, the chief product being γ -methyl- β -benzylideneisoxazolone (m. p. 142°). When treated with hydroxylamine hydrochloride in the cold, ethylic benzylideneacetoacetate yields the hydrochloride of the above methyl benzylideneisoxazolone; this readily loses hydrogen chloride when suspended in alcohol, and, when warmed with a 10 per cent. sodium hydroxide solution, yields a substance which is probably the hitherto unknown labile form of *oximidobenzylideneacetoacetic acid*, $\text{Me}\cdot\text{C}:\text{C}:\text{CHPh}$. It melts at 186°, readily dissolves in alkalis, but is insoluble in water, benzene, and light petroleum. Methyl benzylideneisoxazolone itself does not yield this acid when warmed with alkalis, but is completely decomposed. The *ammonium* salt forms colourless crystals, melts at 194—196°, and is readily soluble in water. The acid may be reconverted into methylbenzylideneisoxazolone either by treatment with an alcoholic solution of hydrogen chloride in the cold, or with aqueous hydrogen chloride at 100°. It is possible that the acid in question may have the constitution $\text{COOH}\cdot\text{CH}\cdot\text{CHPh} \begin{smallmatrix} \text{CMe} = \text{N} \\ > \text{O} \end{smallmatrix}$.

When an alcoholic solution of ethylic benzylideneacetoacetate is treated with free hydroxylamine at the ordinary temperature, a different product is obtained. This melts at 104—106°, and is readily soluble in alcohol, benzene, and light petroleum, but insoluble in water and ether; its constitution has not yet been determined. J. J. S.

A Synthesis of 3 : 5-Methylphenylpyrazole. By CARL GOLDSCHMIDT (*Ber.*, 1895, 28, 2952).—When phenylmethylisoxazole is heated with alcoholic ammonia at 240°, oxygen is replaced by the imido-group, and 3 : 5-methylphenylpyrazole (Sjollema, *Abstr.*, 1894, i, 546) is obtained. C. F. B.

Synthesis of Biazoline Derivatives. By MAX BUSCH (*Ber.*, 1895, **28**, 2635—2647).—Phenylthiocarbazinic acid, in the form of the potassium salt or an ethereal salt, reacts with aldehydes to produce derivatives of thiobiazoline, $S < \begin{smallmatrix} \text{CH}_2 \cdot \text{NH} \\ \text{CH} : \text{N} \end{smallmatrix}$. *Phenylthiobiazoline*

hydrosulphide, $S < \begin{smallmatrix} \text{CH}_2 - \text{NPh} \\ \text{C}(\text{SH}) : \text{N} \end{smallmatrix}$, formed by the action of formaldehyde on the potassium salt of phenylthiocarbazinic acid, crystallises in druses of compact, white plates melting at 112° . It readily dissolves in aqueous alkalis, and is decomposed by boiling with them into formaldehyde and phenylthiocarbazinic acid. *Phenylthiobiazoline bisulphide*, $(\text{C}_6\text{H}_7\text{SN}_2)_2\text{S}_2$, is formed by the action of ferric chloride on the hydrosulphide, and crystallises in lustrous, orange plates, melting at 135° . The bisulphide undergoes a characteristic decomposition when it is heated to 130° , or when its chloroform solution is preserved, the hydrosulphide being formed, together with *phenylisodithiobiazolone*, $\text{NPh} < \begin{smallmatrix} \text{CH} \cdot \text{S} \\ \text{N} - \text{CS} \end{smallmatrix}$. This substance crystallises in narrow,

greenish plates, and melts and decomposes at 190° . It is insoluble in cold alkalis, but dissolves on warming, yielding a solution from which phenylthiocarbazinic acid is deposited on the addition of an acid.

Methylphenylthiobiazoline hydrosulphide, $S < \begin{smallmatrix} \text{CHMe} \cdot \text{NPh} \\ \text{C}(\text{SH}) : \text{N} \end{smallmatrix}$, is prepared from acetaldehyde, and forms large, feathery plates, melting at 132° . The *potassium salt* forms lustrous, white plates, and is readily soluble in water and alcohol. The *bisulphide* crystallises in orange-coloured plates, melting at 140° .

Methylphenylisodithiobiazolone, $\text{NPh} < \begin{smallmatrix} \text{CMe} \cdot \text{S} \\ \text{N} - \text{CS} \end{smallmatrix}$, crystallises in fascicular groups of light yellow plates, which melt at 216° . It does not appear to be converted into methylphenylthiobiazoline hydrosulphide by reduction. It unites with methylic iodide to form a substance of the formula, $\text{C}_9\text{H}_8\text{N}_2\text{S}_2\text{MeI}$, which crystallises in long, lustrous needles, melting at about 180° .

Diphenylthiobiazoline hydrosulphide, $S < \begin{smallmatrix} \text{CHPh} \cdot \text{NPh} \\ \text{C}(\text{SH}) : \text{N} \end{smallmatrix}$, is prepared from benzaldehyde, and crystallises in almost colourless, rhombohedral crystals, which melt at 156.5° . The *sodium salt*, $\text{C}_{14}\text{H}_{11}\text{N}_2\text{S}_2\text{Na} + 3\text{H}_2\text{O}$, forms silvery plates, and the *potassium salt* white needles. *Diphenylthiobiazoline methosulphide*, $\text{C}_{14}\text{H}_{11}\text{SN}_2\text{SMe}$, is obtained by the action of methylic iodide on the hydrosulphide, or by the condensation of benzaldehyde with methylic phenylthiocarbazinate. It crystallises in faintly yellowish-green needles, melting at 93 — 94° . The *bisulphide* is a lustrous brown crystalline powder, melting at 138° .

Diphenylisodithiobiazolone, $\text{NPh} < \begin{smallmatrix} \text{CPh} \cdot \text{S} \\ \text{N} - \text{CS} \end{smallmatrix}$, forms orange-coloured crystals, melting at 223 — 224° .

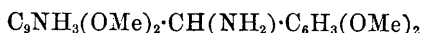
Methylic phenylthiocarbazinate, $\text{NPh}\cdot\text{NH}\cdot\text{CSSMe}$, forms fascicular groups of flat needles, melting at 135° . It dissolves without change in dilute alkalis, and is much more stable than the acid. With formaldehyde, it produces *phenylthiobiazoline methosulphide*, $\text{S} < \begin{array}{c} \text{CH}_2 - \text{NPh} \\ \text{C}(\text{SMe}) : \text{N} \end{array}$, which crystallises in long needles, melting at $34\text{--}35^\circ$. With benzaldehyde, the methylic salt forms the diphenylthiobiazoline methosulphide described above. A. H.

Constitution of Heteroxanthine. By MARTIN KRÜGER and GEORG SALOMON (*Zeit. physiol. Chem.*, 1895, **21**, 169—185)—See this vol., ii, 200.

Water of Crystallisation of Morphine Hydrochloride and of Morphine. By WILHELM GÖHLICH (*Arch. Pharm.*, 1895, **233**, 631—645).—Results of the estimation of water of crystallisation in carefully purified morphine show that at 100° it lost from 0.017 to 2.53 per cent. in weight, and at 120° decomposed slightly, the final loss amounting to 5.89—6.34 per cent. This result is not in agreement with those of Dott (Abstr., 1888, 506) and Dieterich (*Helf. Ann.*, 1888), who record instances of a loss of the total water at 100° , and a loss in weight at 120° of 6.39—6.56 per cent. Estimations made with morphine hydrochloride showed a loss in weight varying from 13.02 to 14.23 per cent. The number calculated from the usually accepted formula, $\text{C}_{17}\text{H}_{19}\text{NO}_3\cdot\text{HCl} + 3\text{H}_2\text{O}$, being 14.38. The author concludes that specimens of morphine hydrochloride, as described by the German Pharmacopœa, containing from 14.5—15 per cent. of water, are of the rarest occurrence. A. L.

Papaveraldoxime. By ROBERT HIRSCH (*Monatsh.*, 1895, **16**, 828—848).—The oxime obtained from Goldschmiedt's papaveraldine (compare Abstr., 1887, 163) consists of two stereoisomerides, of which one crystallises in very slender, microscopic needles, and melts at 235° ; the other crystallises in large, flat prisms, and melts at 254° . From either of these stereoisomerides, by interaction with hydrochloric acid under suitable conditions, the following four hydrochlorides can be prepared:—A *monohydrochloride*, $\text{C}_{20}\text{H}_{20}\text{N}_2\text{O}_5\cdot\text{HCl} + 3\text{H}_2\text{O}$, which forms small, needle-shaped, yellow crystals; a *monohydrochloride*, $\text{C}_{20}\text{H}_{20}\text{N}_2\text{O}_5\cdot\text{HCl} + 10\text{H}_2\text{O}$, which crystallises in colourless, rhombic prisms, sinters at 90° , and melts and decomposes at $220\text{--}225^\circ$; a *dihydrochloride*, $\text{C}_{20}\text{H}_{20}\text{N}_2\text{O}_5\cdot 2\text{HCl} + 12\text{H}_2\text{O}$, which crystallises in yellow, silky, flat needles, melts in its water of crystallisation at $80\text{--}86^\circ$, evolves gas at 109° , again solidifies at a higher temperature, and finally melts and decomposes at $210\text{--}230^\circ$; and a *dihydrochloride*, $\text{C}_{20}\text{H}_{20}\text{N}_2\text{O}_5\cdot 2\text{HCl} + 4\text{H}_2\text{O}$, which crystallises in yellow, rhombic plates, melts at 95° , evolves gas at 110° , and completely decomposes at 210° . All these hydrochlorides when heated at 110° , lose water, or water and hydrogen chloride, and form the same anhydrous monohydrochloride. Attempts to ascertain the configuration of the stereoisomeric papaveraldoximes led to no certain results.

When reduced with sodium amalgam in acid solution, papaverald-oxime is converted into *papaveraldylamine*,



$[(\text{OMe})_2 : \text{N} : \text{CH} = 2 : 3 : 2' : 1' \text{ and } \text{CH} : (\text{OMe})_2 = 1 : 3 : 4]$, a yellowish-brown oil, of vanilla-like odour, which solidifies in an exsiccator to a yellowish-brown mass melting at $80-85^\circ$.

G. T. M.

History of Aconitine. By MARTIN FREUND (*Ber.*, 1895, 28, 2537—2539; compare *Abstr.*, 1895, i, 254).—The author tabulates the results of his analyses of aconitine and some of its derivatives, and compares them with the numbers calculated from the formula proposed by himself, and from that proposed by Wright and adopted by Dunstan. He considers that the results establish the correctness of his formula.

A. H.

Chemistry of Ipecacuanha. By BENJAMIN H. PAUL and ALFRED J. COWNLEY (*Pharm. J. Trans.*, 1894, [3], 25, 111—115, 373—374, 690—692).—The authors' earlier conclusion (*Abstr.*, 1894, i, 155) as to the existence of at least two alkaloids in the substance known as emetine, is confirmed. The separation and properties of these alkaloids are now described. One is a base insoluble in caustic alkalis, and uncrystallisable, for which it is proposed to retain the name of *emetine*; its formula is $\text{C}_{15}\text{H}_{22}\text{NO}_2$; the other, *cephaeline*, $\text{C}_{14}\text{H}_{20}\text{NO}_2$, is soluble in caustic alkali, and obtainable in a crystalline form. These were separated from ipecacuanha by extraction with alcohol, precipitation with basic lead acetate, evaporation of the filtrate to dryness, and treatment of the residue with dilute acid; the solution was mixed with ether, ammonia added in slight excess, and shaken, and from the separated ethereal solution, dilute sulphuric acid took up the emetine, which was precipitated by soda in excess, and subjected to further treatment, in order to entirely remove the other base. The alkaline solution, when acidified and then shaken with ether and ammonia, gave cephaeline. Emetine melts at 68° , is amorphous, strongly alkaline, and colourless, but turns yellow when exposed to light. It is soluble in alcohol, ether, chloroform, or benzene, but only sparingly so in hot light petroleum or in water. Of its salts only the chloride and nitrate could be obtained in a crystalline state. Cephaeline is colourless, but, like emetine, is turned yellow by exposure to light; it is less soluble in ether, and cold light petroleum dissolves it very sparingly, whilst the hot liquid dissolves more of it, but on cooling, deposits it again in a flocculent form. It melts in a capillary tube at $96-98^\circ$, loses weight at 100° when heated in the open, and at 120° is changed, without melting, into a brown substance. The salts of cephaeline much resemble those of the other base, but its platinochloride is of a much darker yellow colour than the corresponding emetine salt.

In the second paper is noted the facility with which the chlorides of each base can be obtained as crystals from solutions containing excess of hydrochloric acid. The authors also criticise certain

results published by Kunz-Krause (Abstr., 1895, i, 118) as quite incompatible with their own observations.

The remaining paper announces the isolation of a third alkaloid from *ipecacuanha*. It exists in relatively small quantity, is characterised by very sparing solubility in ether, and remains in the ammoniacal liquor from which emetin and cephaeline have been extracted by ether. It can be obtained in pale yellow, prismatic crystals which melt at about 138°. Emetine, cephaeline, and their salts are already supplied commercially as medicines.

R. R.

Deliquescent Alkaloid from *Lupinus albus*. By ARTURO SOLDAINI (*Gazzetta*, 25, 1895, i, 352—364).—The high melting hydrobromide of the deliquescent alkaloid obtained from the seeds of *Lupinus albus* melts and decomposes at 233—234°, not at 224—225°, as previously stated (Abstr., 1893, i, 739); it has the specific rotation $[\alpha]_D = -5.6^\circ$ in a 25 per cent. aqueous solution. The *platinochloride*, $(C_8H_{13}NO)_2, H_2PtCl_6 + 2\frac{1}{2}H_2O$, is obtained as a red, crystalline powder, and when anhydrous decomposes at 202—203°; the *aurochloride* decomposes at about 163°, and is reduced by boiling with water. The *hydrochloride* crystallises in thin, prismatic needles which decompose at 165°, is insoluble in cold alcohol, and is laevorotatory in solution. The base seems therefore to be distinct from its isomeride, tropine.

The alcoholic mother liquors obtained during the preparation of the above hydrobromide contain two bases which can be separated by fractional crystallisation of their platinochlorides. One of these yields a *hydrochloride*, soluble in alcohol, which gives a crystalline *platinochloride* $(C_7H_7NO)_2, H_2PtCl_6$; the other yields a crystalline *hydrochloride*, $C_8H_{13}NO, HCl$, melting at 178°, and is insoluble in alcohol.

W. J. P.

Extraction of Alkaloids from the Seeds of *Lupinus albus*. By ARTURO SOLDAINI (*Gazzetta*, 1895, 25, i, 365—380).—The best method of separating the alkaloids from *Lupinus albus* is to treat the aqueous extract of the lupine meal with lime, extract with petroleum, and then to extract the latter solution with dilute hydrochloric acid; the acid solution yields the crude mixture of hydrochlorides on evaporation. The deliquescent alkaloid is less soluble in petroleum than the crystalline one, and the bases may be separated by crystallisation from this solvent. Other methods of extracting the alkaloids are referred to, depending on the use of basic lead acetate, Meyer's reagent, alcoholic hydrochloric acid, and dialysis.

W. J. P.

Formation of Arginine from Proteid Substances. By SVEN G. HEDIN (*Zeit. physiol. Chem.*, 1895, 21, 155—168; compare Abstr., 1895, i, 160).—The substance previously obtained by the author from horny substance is proved to be identical with Schulze and Steiger's arginine (Abstr., 1886, 725). Besides the compounds mentioned by Schulze and Steiger, the author describes the compounds $AgNO_3, C_6H_{14}N_4O_2 + \frac{1}{2}H_2O$, $AgNO_3, C_6H_{14}N_4O_2, HNO_3$, and $C_6H_{14}N_4O_2, 2HNO_3$. The sulphate and oxalate could not be obtained

in a crystalline form. Methods for the preparation of arginine from various sources are given.

Horn yields at least	2.25	per cent, of arginine.
Glue "	2.60	" "
Conglutin yields at least	2.75	" "
Albumin (from yolk of egg) yields at least	2.3	" "
Albumin (from white of egg) yields at least	0.8	" "
Dry blood serum	0.7	" "
Casein	0.25	" "

The arginine is best isolated in the form of the silver salt, $\text{AgNO}_3 \cdot \text{C}_6\text{H}_{11}\text{N}_4\text{O}_2 + \frac{1}{2}\text{H}_2\text{O}$, as this is very sparingly soluble in water, care must be taken that the silver salt $\text{AgNO}_3 \cdot \text{C}_6\text{H}_{11}\text{N}_4\text{O}_2 \cdot \text{HNO}_3$ is not formed, as this is readily soluble. To accomplish this, the phosphotungstic acid precipitate is treated with barium hydroxide, the excess of hydroxide is removed by slightly acidifying with sulphuric acid, and then the sulphuric acid is exactly precipitated with barium hydroxide, and the strongly alkaline filtrate treated with silver nitrate, when the sparingly soluble silver salt is thrown down.

J. J. S.

Anhalonium Lewinji and other Cacti. By LOUIS LEWIN (*Chem. Centr.*, 1895, i, 219—220; from *Arch. Exp. Pathol.*, **34**, 374—391).—Crystals of anhalonine are biaxial and optically active, and belong to the rhombic system. Anhalonine dissolves in water, and gives an alkaline reaction; it is also readily soluble in alcohol, ether, chloroform, &c. The free base may be distilled without undergoing decomposition; it sinters at 74° , and is completely fused at 77.5° . The *hydrochloride*, $\text{C}_{12}\text{H}_{15}\text{NO}_3 \cdot \text{HCl}$, which tastes slightly bitter, melts and decomposes at 254 — 255° ; it is sparingly soluble in cold water, readily in hot, crystallises from water more readily than the alkaloid, the solution being laevorotatory, and is coloured yellow by sulphuric acid; $[\alpha]_D = -40.56^\circ$ in alcoholic solution. Nitric acid gives first a pale red, which changes to a blood red, and, on warming, to a yellow coloration. The *platinochloride*, $(\text{C}_{12}\text{H}_{15}\text{NO}_3)_2 \cdot \text{H}_2\text{PtCl}_6$, is crystalline. In small doses, anhalonine produces reflex irritability, and in larger doses, reflex tetanus; the fatal dose for rabbits is 0.16 — 0.2 gram per kilo, of body weight. The same base may also be obtained from *Anhalonium Jourdanianum*.

J. J. S.

Lithofellic acid. By E. JÜNGER and A. KLÄGER (*Ber.*, 1895, **28**, 3045—3049).—Lithofellic acid, $\text{C}_{20}\text{H}_{36}\text{O}_4$, has been studied by Goebel, Wöhler, Roster, Grattola, and Strecker; it is obtained from gallstones, and when crystallised from alcohol melts at 199° (uncorr.). When an alcoholic solution of lithofellic acid is heated with aqueous barium hydroxide for several hours in a reflux apparatus, ethylic alcohol is eliminated, and an unsaturated acid, $\text{C}_{18}\text{H}_{30}\text{O}_3$, is produced; it crystallises in nacreous scales, and melts at 152° .

Lithofellolactone, $\text{C}_{20}\text{H}_{34}\text{O}_3$, is obtained by heating an alcoholic solution of lithofellic acid with concentrated hydrochloric acid on the

water bath; it is a colourless viscous oil, which boils at $245-248^{\circ}$ under a pressure of 16 mm. The molecular refraction $M = 91.99$. Aqueous barium hydroxide converts the lactone into the unsaturated acid, and this substance also yields a *lactone* which boils at $275-280^{\circ}$ under a pressure of 60 mm. M. O. F.

Emulsin from Fungi. By EMILE F. BOURQUELOT and H. HÉRISSEY (*Compt. rend.*, 1895, **121**, 693—695).—*Aspergillus niger* was cultivated in Raulin's fluid, and when it had fructified, the liquid was drawn off, the residue washed several times with distilled water, and finally allowed to remain in contact with distilled water for several days, the solution of emulsin thus obtained being used for the experiments. This solution hydrolyses amygdalin, salicin, coniferin, arbutin, esculin, helicin, populin, and phloridzin, but has no action on solanin, hesperidin, convallamarin, convolvulin, jalapin, and potassium atractylate. Unlike the emulsin of almonds, it has no hydrolysing action on milk sugar, and it also differs in acting, although very slowly, on populin and phloridzin.

The juice expressed from *Polyporus sulphureus*, &c., which grows on most of the ordinary trees, has similar hydrolysing properties, and acts readily on amygdalin, esculin, arbutin, coniferin, and salicin, but has no effect on milk sugar.

It follows from these and previous observations (Abstr., 1894, ii, 63, 109), that fungi all contain the same emulsin, but the evidence is not yet sufficient to decide whether it is or is not identical with the emulsin from bitter almonds, C. H. B.

Enzymes of Certain Yeasts. By EMIL FISCHER and PAUL LINDNER (*Ber.*, 1895, **28**, 3034—3039).—The authors give details of 24 experiments intended to throw light on the question whether the fermentation of polysaccharides is preceded by hydrolysis. They find that melibiose is hydrolysed by extracts of the yeasts (Frohberg and Saaz) of bottom fermentation; the extracts were prepared by digesting with water at 33° for 20 hours specimens which were dried for three days in air at $20-25^{\circ}$, having been previously drained on porous earthenware. As these types also induce hydrolysis when employed in the moist state, it is evident that the hydrolytic enzyme is not a result of desiccation. Melibiose, however, is indifferent towards the Frohberg and Saaz types of top fermentation yeast, neither the fresh product nor an aqueous extract of the dried yeast effecting hydrolysis of the sugar; this observation contradicts the statement of Scheibler and Mittelmeier (Abstr., 1890, 226), who recorded the complete hydrolysis of melibiose by the agency of invertin, an enzyme which is present in the types indicated. Moreover, the authors have repeated the experiment of Scheibler and Mittelmeier with a negative result, and are led, therefore, to the conclusion that the specimen of invertin which these investigators employed was contaminated with other enzymes of beer yeast.

An aqueous extract of desiccated *Monilia candida* has no action on cane sugar, but the dried product contains a hydrolytic enzyme which is, therefore, insoluble in water; a fresh specimen of the moist yeast

also hydrolyses cane sugar, although less actively than the dried substance. All three preparations of this yeast, however, have a marked hydrolytic action on maltose. *Saccharomyces apiculatus*, whether dry or fresh, is without hydrolytic action on cane sugar.

In the course of these experiments, thymol and toluene have been employed as anæsthetic agents to prohibit fermentation.

M. O. F.

Liquefaction and Saline Digestion of Gelatin. By A. DASTRE and N. FLORESCO (*Compt. rend.*, 1895, **121**, 615—617).—The liquefaction of gelatin, or loss of the power of gelatinisation, is brought about by the prolonged or repeated action of boiling water, the brief action of water at a high temperature, the action of certain saline solutions, and also, as is well known, by the action of liquefying bacteria, and by gastric or pancreatic digestion.

Gelatinisation begins to be apparent with solutions containing 0.75 part of gelatin in 100; solutions containing 5 to 10 parts per 100 are strong solutions in which the phenomena can be easily followed, whilst solutions containing 2.3 parts per 100 may be regarded as of medium concentration.

The liquefaction is due to the conversion of the gelatin, by combination with water, into gelatose or protogelatose, which is characterised by the fact that it will not gelatinise and is not precipitated by a saturated solution of sodium chloride, complete liquefaction corresponding with complete conversion into gelatose. The same change is produced by liquefying bacteria.

Contrary to the usual belief, comparatively short exposures of gelatin to such temperatures as 110—120° causes a partial conversion of gelatin into gelatose with consequent loss of gelatinising power, and there is little doubt that any contact with warm water does affect the gelatin, although the effect may not be at once appreciable.

In contact with certain salts, such as alkali chlorides or iodides, gelatin gradually loses its power of solidifying. With solutions containing only 1 part of salt per 100, the effect on the gelatin is shown by the greater time required for gelatinisation and the lower consistency of the jelly. With 10 parts of salt per 100 liquefaction is complete, and the gelatin is entirely converted into gelatose whatever the proportion of gelatin used. It is noteworthy, however, that with alkali fluorides, the change is never complete. To this phenomenon the authors give the name *saline digestion*, because it is identical in its results with gastric and pancreatic digestion, and is produced under similar conditions, that is to say, by prolonged contact at a moderate temperature, such as 46°, but not by short exposure to a high temperature such as 100—120°.

C. H. B.

Organic Chemistry.

Sodium Nitroferrocyanide. By KARL A. HOFMANN (*Zeit. anorg. Chem.*, 1896, **11**, 31—36; see also this vol., i, 69).—A compound, $\text{Fe}(\text{CN})_5\text{Na}_3\text{SO}_3 + 9\text{H}_2\text{O}$, is obtained by adding sodium nitroferrocyanide (20 grams) to a 40 per cent. solution of sodium hydrogen sulphite (50 grams), neutralising with sodium hydroxide, and adding 20 c.c. more of a 10 per cent. solution of sodium hydroxide. The intensely yellowish-red solution is evaporated in a vacuum over sulphuric acid, and the red crystals of the compound, after separating them from the sodium sulphate, recrystallised, taking care that the solution is not heated above 30° . It crystallises in long, thin, pale yellow needles, does not yield ammonia when heated with sodium hydroxide, gives a yellowish-green solution with hydrochloric acid, and then evolves sulphurous anhydride, a beautiful red coloration when boiled with hydroxylamine and sodium hydroxide, a bluish-white precipitate with ferrous sulphate, and a dark blue precipitate with ferric chloride. It remains entirely unaltered when treated with sodium hydrogen sulphite. When treated with iodine, the ferro-compound is converted into a ferri-compound, and with permanganate in acid solution, it yields a ferri-compound and sulphate. When treated with hydrogen peroxide, it remains for the most part unaltered. When treated with nitrous acid or nitric oxide, it yields sodium nitroferrocyanide. E. C. R.

Preparation of Platinocyanides. By ARNULF SCHERTEL (*Ber.*, 1896, **29**, 204—205).—These salts can be prepared very easily by dissolving well washed and freshly precipitated platinum sulphide in a solution of the corresponding cyanide, and concentrating the colourless solution; $\text{PtS}_2 + 5\text{KCN} = \text{K}_2\text{Pt}(\text{CN})_4 + \text{K}_2\text{S} + \text{KCNS}$. $\text{K}_2\text{Pt}(\text{CN})_4 \cdot 3\text{H}_2\text{O}$, and $\text{BaPt}(\text{CN})_4$, were so prepared. If commercial potassium cyanide, which at the present time (in England also?) is nearly half sodium cyanide, is used, crystals of the salt $\text{KNaPt}(\text{CN})_4 \cdot 3\text{H}_2\text{O}$ are obtained, and, from the mother liquor of these, crystals of $\text{Na}_2\text{Pt}(\text{CN})_4$. C. F. B.

Organic Compounds containing Quadrivalent Oxygen. By F. ZECCHINI (*Gazzetta*, 1895, **25**, ii, 58—63).—Friedel (*Abstr.*, 1875, 1245) obtained a liquid boiling at -1° to -3° by the action of dry hydrogen chloride on dry methylic alcohol at -20° which was so unstable at ordinary temperatures that it could not be ascertained whether it consisted of the compound $\text{MeOH} \cdot \text{HCl}$, containing quadrivalent oxygen. The author has repeated Friedel's experiment, and has also investigated the action of methylic iodide on methylic ether at -18° ; in the latter case, a liquid is obtained by distillation, which boils at 0° to 1° , and contains iodine, but does not lend itself to further examination.

Determinations of the depression of the freezing points of various
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solvents by mixtures of methylic ether with hydrogen chloride or methylic iodide seem to indicate that at the temperature of the freezing solvent no combination exists. W. J. P.

Rhodinol or Geraniol. By HUGO ERDMANN and P. HUTH (*J. pr. Chem.*, 1896, [2], 53, 42—46; compare Tiemann and Semmler, *Abstr.*, 1895, i, 646).—Rhodinol and geraniol will combine with dibasic acids to form acid ethereal salts; such a compound with camphoric acid has been analysed.

Rhodinol diphenylurethane, $\text{NPh}_2\cdot\text{CO}\cdot\text{OC}_{10}\text{H}_{17}$, crystallises in long, silky, felted needles, and melts at $83\text{--}84^\circ$. This compound has been obtained from rhodinol, geraniol, and reuniol, as well as from German and Turkish rose oil. It is thus proved that "reuniol" is identical with rhodinol, so that this name must be erased from scientific literature (compare Hesse, *Abstr.*, 1895, i, 186).

A. G. B.

Composition of Wool Fat. By L. DARMSTAEDTER and ISAAC LIFSCHÜTZ (*Ber.*, 1895, 28, 3133—3135).—On hydrolysing wool fat, the authors obtained an *alcohol*, $\text{C}_{10}\text{H}_{20}\text{O}$, which melts at $105\text{--}109^\circ$, and appears to be unsaturated; an *alcohol*, $\text{C}_{11}\text{H}_{22}\text{O}$, which crystallises in needles, and melts at $82\text{--}87^\circ$, has been also isolated. The authors regard these alcohols as lower homologues of lanolinic alcohol (Marchetti, *Abstr.*, 1895, i, 408).

M. O. F.

Reduction of Pseudonitroles to Ketoximes. By ROLAND SCHOLL and KARL LANDSTEINER (*Ber.*, 1896, 29, 87—90).—In order to throw light on the structure of the pseudonitroles, the authors have submitted propylpseudonitrole to reduction; employing free hydroxylamine and potassium hydrosulphide, they obtained acetoxime in each case.

M. O. F.

Pseudonitroles and Dialkyldinitromethanes. By GEORG BORN (*Ber.*, 1896, 29, 90—102; compare the foregoing abstract, and *Abstr.*, 1895, i, 445).—The resemblance between nitrosobenzene and the pseudonitroles, and the reduction of the latter to ketoximes with hydroxylamine or potassium hydrosulphide, lead the author to advocate V. Meyer's expression for the structure of pseudonitroles, which represents them as nitro-nitroso-compounds; moreover, oxidation of the pseudonitroles gives rise to dialkyldinitromethanes, and these also, when reduced, yield ketoximes.

Diethyldinitromethane, $\text{CET}_2(\text{NO}_2)_2$, is obtained by oxidising amyl- β -pseudonitrole with chromic acid in glacial acetic acid; it is a colourless liquid, which boils at $207\text{--}208^\circ$ under a pressure of 723 mm., and has an agreeable, camphor-like odour.

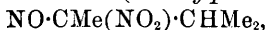
Ethylpropylpseudonitrole (amyl- α -pseudonitrole),



is prepared by submitting an ethereal solution of methylpropylketoxime to the action of a current of nitric peroxide; it is a deep blue oil, which becomes green and decomposes in sunlight, and yields brown gas when heated at 59° . Oxidation, with chromic acid, in glacial acetic acid solution, gives rise to *methylpropyldinitromethane*, a colourless oil,

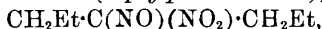
which boils at $207\cdot5$ — $209\cdot5^\circ$ under a pressure of 723 mm., and has a pleasant odour resembling that of camphor.

as-*Dimethylpropylpseudonitrole (isoamylpseudonitrole)*,



is a blue oil, which decomposes at 60° ; on oxidation it yields *methyl-isopropyldinitromethane*, a pale green liquid, which solidifies in a mixture of ice and salt, and boils at 205 — 207° under a pressure of 724 mm.

Diethylpropylpseudonitrole (heptylpseudonitrole),

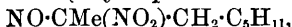


separates from ether in white rhombohedra, which melt, forming a blue liquid, and evolving gas, at 72 — 73° ; during the preparation of this substance, the nitrimine is formed (compare *loc. cit.*), together with a mixture of dipropyl ketone and *dipropyldinitromethane*. The latter substance is also obtained by the oxidation of diethylpropylpseudonitrole; it is a colourless oil, which has an agreeable, camphor-like odour, and boils at 220 — 221° . Oxidation of the pseudonitrole is also attended with regeneration of dipropyl ketone, and reduction with free hydroxylamine or alkali hydrosulphides gives rise to dipropylketoxime.

Tetramethylpropylpseudonitrole, $\text{CHMe}_2\cdot\text{C}(\text{NO})(\text{NO}_2)\cdot\text{CHMe}_2$, is a pungent, blue oil, which decomposes at 54° ; oxidation converts it into *diisopropyldinitromethane*, which boils and partly decomposes at 203 — 207° under a pressure of 717 mm. Diisopropyl ketone is also produced by oxidation of the pseudonitrole.

Methyl α -ethylpropyl ketoxime, $\text{CHEt}_2\cdot\text{CMe}\cdot\text{NOH}$, is a colourless liquid, which boils at 186 — $188\cdot5^\circ$ (uncorr.) under a pressure of 712 mm. The action of nitric peroxide gives rise to a green oil consisting of the impure pseudonitrole, which decomposes at 67° , and when oxidised yields *methyl- α -ethylpropyldinitromethane*; this substance is a yellow oil, which boils at 211 — 219° under a pressure of 722 mm.

Amylpropylpseudonitrole (octyl- α -pseudonitrole),



obtained from methyl hexyl ketoxime, is a blue oil, which decomposes at 53 — 55° , and solidifies in a freezing mixture; oxidation converts it into *methylhexyldinitromethane*, a yellowish-brown oil, which decomposes at 180° , yielding methyl hexyl ketone. M. O. F.

β -Ethoxybutylamine and γ -Ethoxybutylamine. By S. BOOKMAN (*Ber.*, 1895, **28**, 3111—3121; compare *Abstr.*, 1895, i, 190).—When ethylic chloro-*sec*-butylic ether, $\text{CH}_2\text{Cl}\cdot\text{CHEt}\cdot\text{OEt}$, is heated in sealed tubes with alcoholic ammonia for three hours at 140° , β -ethoxybutylamine and di- β -ethoxybutylamine are produced.

β -*Ethoxybutylamine*, $\text{OEt}\cdot\text{CHEt}\cdot\text{CH}_2\cdot\text{NH}_2$, is a highly refractive liquid, which boils at 139 — 141° , and has a sp. gr. = $0\cdot8505$ at 16° ; it readily absorbs atmospheric carbonic anhydride, and dissolves sparingly in water. The *hydrochloride* crystallises in white plates, and the *platinochloride* is extremely soluble in water; the *picrate* crystallises from hot water in lemon-yellow needles, and melts at 156° . The *phenylthiocarbamide* crystallises in lustrous, white needles, and melts at 94° .

β-Chlorobutylamine is obtained in the form of the *hydrochloride* by heating *β*-ethoxybutylamine (2 grams) with fuming hydrochloric acid (20 c.c.) for $2\frac{1}{2}$ hours at $150-160^\circ$; the *picrate* melts at 142° , and the *platinochloride* crystallises in yellow leaflets. When heated in sealed tubes at 100° with aqueous alkali, the hydrochloride of the base yields *α*-crotylamine (compare Abstr., 1892, 33).

β-Bromobutylamine hydrobromide is formed when *β*-ethoxybutylamine is heated with hydrobromic acid; the *picrate* melts at $150-151^\circ$, and decomposes at 210° . When an aqueous solution of the hydrobromide is agitated with alkali and benzoic chloride, the *benzoyl* derivative is produced, and this yields *β-μ-ethylphenylloxazoline*,

$\text{CH}_2 < \begin{array}{c} \text{CHEt} \cdot \text{O} \\ \text{N} = \text{C} \text{Ph} \end{array}$, when submitted to the action of a current of steam while in contact with alkalis. The *picrate* of this base crystallises in long needles, and melts at 168° .

β-Ethylthiazoline α-hydrosulphide, $\text{CH}_2 < \begin{array}{c} \text{CHEt} \cdot \text{S} \\ \text{N} = \text{C} \cdot \text{SH} \end{array}$, is obtained by the action of carbon bisulphide on the hydrobromide of *β*-bromobutylamine in presence of alkali; oxidation with bromine water converts this substance into the *β-ethyltaurine*, $\text{HSO}_2 \cdot \text{CHEt} \cdot \text{CH}_2 \cdot \text{NH}_2$, which crystallises from water, and decomposes at 285° .

Di-β-ethoxybutylamine, $\text{NH}(\text{CH}_2 \cdot \text{CHEt} \cdot \text{OEt})_2$, is a feebly refractive liquid, which boils at 230° , and has a sp. gr. = 0.87 at 16° . The *hydrochloride* is white; the *aurochloride* is orange, and melts at 113° ; the *picrate* is yellow, and melts at $83-85^\circ$; and the *nitrosamine* is a viscous oil which boils at 259° ; when heated with fuming hydrochloric acid, the base yields a substance which is probably *di-β-chlorobutylamine*, the *aurochloride* of which melts at $170-171^\circ$. An unsaturated base (probably consisting of *dicrotylamine*) is obtained on heating *di-β-ethoxybutylamine* with hydrobromic acid at 140° , and distilling with potash the hydrobromide thus obtained; the *picrate* crystallises in yellow prisms, melts at $172-173^\circ$, and decomposes at 225° .

γ-Ethoxybutylamine is obtained by reducing the nitrile of *γ*-chlorobutyric acid with sodium and alcohol, butylamine being formed at the same time; it boils at 148° , and has an ammoniacal odour. The *oxalate* melts at $198-200^\circ$, the *platinochloride* at 190° , and the *thiocarbamide* at $91-92^\circ$. Fuming hydrochloric acid at 150° converts the base into ethylic chloride and *γ*-chlorobutylamine. M. O. F.

Alkyl Derivatives of Ethylenediamine. By PAUL SCHNEIDER (*Ber.*, 1895, 28, 3072-3078; compare Hinsberg, this vol., i, 47).—Diphenylsulphonethylenediamine, $\text{C}_2\text{H}_4(\text{NH} \cdot \text{SO}_2\text{Ph})_2$, was prepared by Hinsberg's reaction (Abstr., 1892, 64) from ethylenediamine and benzenesulphonic chloride, and was converted by warming with methylic iodide and aqueous-alcoholic soda into *diphenylsulphonedimethylethylenediamine*, $\text{C}_2\text{H}_4(\text{NMe} \cdot \text{SO}_2\text{Ph})_2$, melting at 131° . This, by heating with strong hydrochloric acid, was hydrolysed, yielding *dimethylethylenediamine*, $\text{C}_2\text{H}_4(\text{NHMe})_2$, the *hydrochloride* of which melts and decomposes at $235-236^\circ$; the orange-red *platinochloride*, with $4\text{H}_2\text{O}$, darkens when anhydrous at 205° , and melts and decomposes at

209°; the yellow *aurochloride* crystallises with H_2O ; the yellow *picrate* melts at 215—216°. The base itself, a diacid one, was prepared by distilling the hydrochloride with powdered potassium hydroxide and soda-lime from a copper retort; it boils at 119°, and has a sp. gr. = 0.848 at 4°, and 0.828 at the ordinary temperature (water at 4° = 1); it attracts water and carbonic anhydride from the air, and, with nitrous acid in concentrated solution, it yields yellowish-green *dimethylethylenedinitrosamine*, $\text{C}_2\text{H}_4(\text{NMe}\cdot\text{NO})_2$, melting at 60—61°, showing that it is a di-secondary, and not a primary-tertiary base.

The analogous ethyl derivatives were also prepared before the publication of Hinsberg's paper. Diethylethylenediamine boils at 149—150°; the orange-red *platinochloride* melts at 223—224°, and the *aurochloride* at 220°; the *dinitrosamine* was obtained as a yellowish-green oil which decomposed on heating.

Ethylenediamine forms a *mercurochloride*, $\text{C}_2\text{H}_4(\text{NH}_2)_2\cdot 2\text{HCl}\cdot\text{HgCl}_2$, which melts at 297°.

Hexamethylethylenediammonium chloride, $\text{C}_2\text{H}_4(\text{NMe}_3\text{Cl})_2$, was prepared by the action of silver chloride on the iodide (Hofmann, *Jahresbericht*, 1859, 386); the *platinochloride* blackens at 260°, and melts and decomposes at 286°; the *picrate* melts at 262°.

C. F. B.

Lysidine. By ALBERT LADENBURG (*Ber.*, 1895, 28, 3068—3070).—

If lysidine, $\text{C}_2\text{H}_4\langle\begin{smallmatrix} \text{NH} \\ \text{N} \end{smallmatrix}\rangle\text{CMe}$ (*Abstr.*, 1895, i, 73), is shaken with benzoic chloride and potassium carbonate, it yields *acetodibenzoethylenediamine*, $\text{NHBz}\cdot\text{C}_2\text{H}_4\cdot\text{NAcBz}$, melting at 113—114°, and when this is shaken with sodium hydroxide, it is converted into dibenzoethylenediamine, $\text{C}_2\text{H}_4(\text{NHBz})_2$, melting at 244°; this is very sparingly soluble in alcohol, and its formation can be used to detect lysidine in a 0.1 per cent. solution (which must of course contain no ethylenediamine); it is only necessary to shake the solution with benzoic chloride and sodium hydroxide.

When lysidine hydrochloride is submitted to dry distillation, it is decomposed into ammonium chloride and methylic cyanide; acetylene, or a polymeride of that substance, is presumably formed in addition, but no proof of this could be obtained.

C. F. B.

Preparation of Ethereal Salts. By EMIL FISCHER and ARTHUR SPEIER (*Ber.*, 1895, 28, 3252—3258).—The experiments detailed below show that the use of mineral acid in excess is frequently unnecessary, and sometimes decreases the yield of ethereal salt. The yield of ethylic benzoate prepared by the ordinary method with hydrogen chloride and sulphuric acid is 73 and 76 per cent. respectively, but, when benzoic acid is boiled with alcohol (2 parts) containing hydrogen chloride (3 per cent.), the yield is 76 per cent., and with sulphuric acid (10 per cent.), after heating during three hours, the yield is 90 per cent. of the theoretical. In the following table, the yield refers to the purified salt; only the authors' best results are given, but these could probably often be improved if the conditions were modified. Absolute ethylic alcohol was always employed, and the solution boiled, unless otherwise stated.

Acids.	Alcohol.	Mineral acid.	Hours boiled.	Yield per cent.
α -Naphthoic, 10 grams.....	30 grams	0.9 gram HCl	4	74.8
Phenylacetic, 10 ".....	30 "	0.9 " "	4	87.0
Cinnamic, 15 grams.....	45 "	4.5 " H_2SO_4	5	89.7
Crotonic, 5 grams.....	15 "	1.5 " "	4	54.3
Mandelic, 5 grams.....	15 "	0.15 " HCl	4	67.5
Salicylic, 10 ".....	30 "	6.0 " H_2SO_4	4	54.0
" 10 ".....	100 "	5.0 " HCl	4	54.5†
Glycollic, 10 ".....	30 "	0.3 " "	4	65.8
Levulinic, 10 ".....	30 "	0.3 " "	4	76.5
Succinic, 10 ".....	50 "	0.5 " "	4	73.9
" 10 ".....	40 "	0.4 " H_2SO_4	4	73.9
Fumaric, 10 ".....	40 "	0.4 " HCl	4	68.2
Citric, hydrated, 10 grams...	40 "	1.2 " "	4	67.3
Phthalic, anhydride, 10 grams	50 "	1.5 " "	4	63.3
Terephthalic, 3 grams.....	18 "	0.54 " "	50*	74.7
Malic, 10 grams.....	40 "	0.4 " "	4	70.5
Tartaric, 20 grams.....	80 "	0.8 " "	4	72.8
Mucic, 5 grams.....	25 "	0.75 " "	12	47.3
" 5 ".....	25 "	0.75 " "	24*	90.8†

A considerable loss of ethylic glycolate occurs, on account of its great volatility; it has not been previously prepared from the free acid. The use of mineral acid is not advantageous in the preparation of ethylic pyruvate; the best yield is obtained by heating the acid and alcohol at 100° . The use of a sealed tube for the etherification of terephthalic acid is necessary, as, with a reflux apparatus, violent bumping occurs. Limpricht has stated that mucic acid is not etherified by the action of hydrochloric acid, or sulphuric acid, and alcohol; the methylic salt, prepared in a sealed tube, is obtained at once in a high state of purity. These results show that, in order to obtain the best yield, the quantity of mineral acid used for the etherification must be determined for each acid separately. The advantages of dilute acid are as follows: it is easier to use, the product is more readily purified, loss of alcohol is reduced to a minimum, and compounds may be prepared which are attacked by concentrated mineral acids.

J. B. T.

Diethylacetylenic Dipropionate. By FRANCESCO ANDERLINI (*Gazzetta*, 1895, 25, ii, 46—57).—Klinger and Schmitz (Abstr., 1891, 890) showed that sodium acts on butyric and isovaleric chlorides, with the formation not of dibutryl and diisovaleryl, but of dipropylacetylenic dibutyrates and diisobutyrylacetylenic diisovalerates; the reaction proceeds in the same way with propionic chloride. Sodium wire acts slowly on an ethereal solution of propionic chloride, and the ethereal liquid, on distillation, yields a yellow oil, which, after washing with sodium carbonate, drying with potassium carbonate, and distilling under reduced pressure, gives *diethylacetylenic dipropionate*, $COEt \cdot O \cdot C \equiv C \cdot O \cdot COEt$. It is a faintly odorous, yellowish,

* Heated at 100° in a sealed tube.

† Methylic salt.

oily liquid, which boils at 108—109° under a pressure of 10 mm., is decolorised on exposure to light, and has the densities 1·00837 at 5·6°/4° and 0·99032 at 28·1°/4°. On hydrolysis by hot alcoholic potash, it behaves in a manner analogous to its higher homologues, and yields *propyroïn*, COEt·CHEt·OH, which can be purified by distillation under reduced pressure; this boils at 132—135° under 227 mm. pressure, and has a density of 0·94288 at 16·6°/4°.

The densities of butyroïn and isovaleroïn are 0·9466 and 0·90256 at 16·7°/4° and 17·4°/4° respectively. Dipropylacetylenic dibutyrate has a sp. gr. = 0·94324 at 20°/4°, and diisobutylacetylenic diisovalerate a sp. gr. = 0·91320 at 20°/4°. All the above substances give normal molecular weights by the cryoscopic method. W. J. P.

Hydroxylamidoisobutyric acid. By GUSTAV MÜNCH (*Ber.*, 1896, **29**, 62—65).—When pure acetoxime, $\text{CMe}_2\text{N}\cdot\text{OH}$, is allowed to remain with a slight excess of anhydrous hydrogen cyanide in closed vessels at the ordinary temperature, monoclinic crystals of *hydroxylamidoisobutyronitrile*, $\text{CN}\cdot\text{CMe}_2\text{NH}\cdot\text{OH}$, are formed; this substance melts at 98·5°; its *hydrochloride* melts and decomposes at 210°. The best way of hydrolysing it, is to dissolve it in concentrated sulphuric acid, dilute with two-thirds as much water, and heat for a few hours at 80—85°; in this way, *hydroxylamidoisobutyric acid*,



is obtained, melting and decomposing at 168°.

C. F. B.

Optically Active Valeric acid. By O. SCHÜTZ and WILHELM MARCKWALD (*Ber.*, 1896, **29**, 52—59).— α -Methylbutyric acid, $\text{CHMeEt}\cdot\text{COOH}$, was synthesised by Conrad and Bischoff's method (*Annalen*, **204**, 151), and an endeavour was made to separate it into its optically active components by fractional crystallisation of its brucine salt—the only salt amongst those tried that was at all suitable for the purpose. Even then the separation was extremely difficult; for the two optical isomerides, although hemimorphous, are not enantiomorphous, as usual, but are actually isomorphous with each other and with the inactive (racemic) salt. The *l*-acid, the brucine salt of which is the less soluble, was finally obtained with a rotation $\alpha_D = -16\cdot3^\circ$ in a tube 100 mm. long, which rotation was not increased by further crystallisation, but the *d*-acid could not be obtained with a greater rotation than $\alpha_D = +10^\circ$, and doubtless still contained some *l*-acid admixed. The brucine salts of both acids have the composition $\text{C}_5\text{H}_{10}\text{O}_2\cdot\text{C}_{23}\text{H}_{28}\text{N}_2\text{O}_4 + 3\text{H}_2\text{O}$; that of the *l*-acid softens at 95° and melts at 100°; when anhydrous, it softens at 80° and melts at 88° to a turbid liquid, which becomes clear at 94°; that of the *d*-acid softens at 93° and melts at 95°; when anhydrous, it melts at 60—63°. The *l*-acid is like the inactive acid, in that it boils at 173—174°, does not solidify at -80°, has sp. gr. 0·954 at 0°/0°, 0·934 at 20°/4°, and 0·926 at 30°/4° (inactive, 0·936 at 20°/4°), and forms very similar salts. The calcium salt, with 5H₂O, or 1½H₂O after drying in the air for two months, and the zinc salt of the *l*-acid are less soluble in hot than in cold water; 100 c.c. of an aqueous solution of the silver salt at 16°

contains 0.675 gram of the salt, whereas 100 parts of water dissolves 1.182 parts of the corresponding inactive salt at 20°. The rotation of the *l*-acid at 20° and 30° is given for light of different wavelengths.

An attempt was made to prepare from the active acid, by the action of bromine at a low temperature in the presence of phosphorus, an active acid, $\text{CBrMeEt}\cdot\text{COOH}$, which would have no hydrogen atom united directly with the asymmetric carbon atom. The substance actually obtained was optically inactive, and identical with the monobromo-acid prepared by Böcking (*Annalen*, **204**, 23) by brominating inactive methylethylacetic acid at 150–160°; it is an oil, and boils at 140° under 50 mm. pressure.

C. F. B.

Action of Sulphur on Unsaturated Fatty Compounds. By ROBERT HENRIQUES (*Zeit. angew. Chem.*, 1895, 691–692).—The author's experiments prove that a true combination of sulphur with fats or fatty acids exists. In one experiment, colza oil was fused with excess of sulphur for three hours, and after cooling, the liquid was filtered. It showed, on analysis, 3.99 per cent. of sulphur. A portion of it was now saponified with cold alcoholic soda in the presence of light petroleum, and the fatty acids were separated by hydrochloric acid. Some of the sulphur apparently existed in a free or loosely combined state, and had formed sodium sulphide, but the bulk was combined with the fatty acids, which showed 3.23 per cent. of sulphur. Treatment with hot alcoholic soda, however, removed the greater part of this sulphur, but the fatty acids still retained 1.93 per cent.

The experiment with sulphuretted linseed oil was more satisfactory. A sample, containing 8.53 per cent. of sulphur, yielded, by the cold process, fatty acids containing 6.62 per cent.; by the hot process, acids containing 5.58 per cent. of sulphur. Brown "*factis*" was next tried. A sample containing 15.48 per cent. of sulphur, gave, by the cold process, acids containing 15.20 per cent.; by the hot process, acids containing 14.14 per cent. of sulphur.

L. DE K.

Preparation of some Cobalti-Compounds. By S. P. L. SÖRENSEN (*Zeit. anorg. Chem.*, 1896, **11**, 1–5).—Potassium cobaltioxalate, $\text{K}_6\text{Co}_2(\text{C}_2\text{O}_4)_6\cdot 6\text{H}_2\text{O}$, previously obtained in small quantities by Kehrman (*Abstr.*, 1891, 1189), is easily prepared in the following manner: A mixture of cobalt carbonate (25 grams), a saturated solution of potassium oxalate (250 c.c.), and a saturated solution of oxalic acid (200–230 c.c.), is heated on the water bath until all the cobalt carbonate is dissolved. It is then cooled to 40°, oxidised with lead peroxide (30 grams), and then cooled and gradually mixed with acetic acid (50 c.c.), and filtered. The filtrate is precipitated, stirring constantly, with successive portions of alcohol, filtered, and the precipitate washed with absolute alcohol. The product is dissolved in the least possible quantity of water and again precipitated with alcohol. About 55–60 grams of the pure salt is obtained.

Ammonium cobaltioxalate is prepared in a similar way, but using a more concentrated solution, as the salt is much more soluble both in

water and in alcohol. The author is engaged in studying the properties of these salts, and especially their behaviour towards ammonia.

E. C. R.

Hydrolysis of the Alkyl Substitution Derivatives of Ethylic Malonate. By EDVARD I. HJELT (*Ber.*, 1896, 29, 110—111).—When the alkyl substitution derivatives of ethylic malonate are treated at 16° with a decinormal solution of soda in 96 per cent. alcohol, 1/20 of a gram-molecule of the compound being present per litre, it is found that, without exception, the dialkyl derivatives are much more slowly hydrolysed than the monalkyl derivatives. The rate of hydrolysis, moreover, does not appear to depend on the strength of the acid.

The experiments included ethylic malonate, together with the following derivatives: ethyl-, propyl-, isopropyl-, isobutyl-, allyl-, benzyl-, dimethyl-, diethyl-, diallyl-, and allylisopropyl-. The author considers that these phenomena are to be explained by stereochemical considerations.

A. H.

Interconversion of Optical Antipodes. By PAUL WALDEN (*Ber.*, 1896, 29, 133—138).—The author has previously shown (this vol., i, 139) that asparagine can be converted into *l*-bromosuccinic acid by the action of bromine and nitrous oxide, and into *d*-bromosuccinic acid by treating the malic acid prepared from the asparagine with phosphorus pentabromide. By passing nitrous oxide into a sulphuric acid solution of aspartic acid, to which potassium bromide and bromine have been added, *l*-bromosuccinic acid separates, and may be extracted with ether. A good yield is got thus, but a practically theoretical yield of *l*-chlorosuccinic acid may be obtained by passing chlorine and nitrous oxide into a hydrochloric acid solution of aspartic acid in the cold, the acid being extracted with ether. Both *lævo*- and *dextro*-isomerides are thus obtained from the same source at the ordinary temperature.

After a number of abortive attempts, the *l*-bromosuccinic acid was converted into *l*-malic acid by warming its aqueous solution with freshly precipitated silver oxide; *d*-chlorosuccinic acid was similarly converted into *d*-malic acid. Both samples of malic acid had the proper specific rotations. It was further shown that *d*-malic acid can be converted into its *l*-isomeride in the same way that the latter can be converted into the former.

Consequently, starting with *l*-malic acid, *d*-chlorosuccinic acid can be directly prepared, and by displacing the chlorine in this by hydroxyl, *d*-malic acid, the optical isomeride of the material used, is obtained; this may then be converted into *l*-chlorosuccinic acid, which, in turn, yields *l*-malic acid again.

W. J. P.

A Homologue of Asparagine and Derivatives of Homo-aspartic acid. By WILHELM KÖRNER and ANGELO MENOZZI (*Real. Accad. Lincei*, 1893, ii, 368—374; compare *Abstr.*, 1890, 869).—On heating the diethylic salts of citraconic, mesaconic, and itaconic acids in sealed tubes with alcoholic ammonia at 105—110°, derivatives of

the same homoaspartic acid, $\text{COOH} \cdot \text{CMe}(\text{NH}_2) \cdot \text{CH}_2 \cdot \text{COOH}$, are obtained.

Ethylic citraconate, by this treatment, deposits *homoaspartic diamide*, $\text{C}_5\text{H}_{11}\text{N}_3\text{O}_2$; it crystallises in small needles melting at 175° , and when boiled with barium hydroxide, evolves ammonia and loses its alkaline reaction, yielding barium homoaspartate. The liquid from which the diamide separates contains *homoasparagine*,



which crystallises in large, efflorescent, orthorhombic plates, containing $2\text{H}_2\text{O}$, and is optically inactive; $a : b : c = 0.695 : 1 : 2.414$. It gives off ammonia when boiled with alkalis, and has feebly acid properties; the *copper* salt $(\text{C}_5\text{H}_9\text{N}_2\text{O}_3)_2\text{Cu} \cdot \text{H}_2\text{O}$, crystallises in small, blue tablets, which lose water at 130 — 135° , becoming violet.

Diethylic mesaconate, or diethylic itaconate, when heated with alcoholic ammonia, deposits *homoaspartic monamide*, $\text{C}_5\text{H}_9\text{N}_2\text{O}_2$, which crystallises in colourless needles melting at 195° . On boiling with barium hydroxide, ammonia is evolved, and a barium salt is formed, from which *homoaspartic acid* may be obtained; it crystallises in transparent, hemihedral, orthorhombic prisms with $1\text{H}_2\text{O}$, and, when anhydrous, melts at 166.5 — 167° ; $a : b : c = 0.658 : 1 : 1.211$. The solution is optically inactive, but the crystals are hemihedrally developed, so that the two active isomerides may be separated.

W. J. P.

Preparation of $\alpha\alpha$ -Dimethylglutaric acid from the Corresponding Hydroxy-acid. By SERGIUS REFORMATSKY (*Ber.*, 1895, 28, 3262—3265; compare this vol., i, 128).— β -Hydroxy- $\alpha\alpha$ -dimethylglutaric acid, $\text{COOH} \cdot \text{CHMe} \cdot \text{CH}(\text{OH}) \cdot \text{CHMe} \cdot \text{COOH}$, is prepared by the action of ethylic bromopropionate and ethylic formate on zinc; it crystallises in needles, and melts at 135 — 136° , but the liquid only becomes transparent at 141° . The electrolytic conductivity $k = 0.0108$, $\mu_\infty = 350$. The *ethylic* salt is oily, almost colourless, boils at 270 — 271° , and is most readily converted into the acid by means of barium hydroxide. The *anhydride* melts at 108 — 109° , and is crystalline. A *calcium* salt has also been prepared. When reduced by means of hydriodic acid, the hydroxy-acid is converted into fumaroid $\alpha\alpha$ -dimethylglutaric acid, but it melts at 145 — 145.5° , not at 140 — 141° , as stated by Auwers (*Abstr.*, 1895, i, 209), no maleinoid acid is formed. Auwers (*loc. cit.*) referred the production of this isomeride by Zelin-sky's method, to the fact that it is prepared from ethylic α -cyanopropionate, which contains an asymmetric carbon atom; as ethylic α -bromopropionate also contains one, this view requires modification.

J. B. T.

Reactions of Tartaric acid and Alkali Tartrates. By LOUIS MAGNIER DE LA SOURCE (*Compt. rend.*, 1895, 121, 774—776).—Potassium hydrogen tartrate is readily soluble in a concentrated solution of potassium acetate, and hence a small quantity of tartaric acid added to such a solution produces no precipitate. Precipitation, however, takes place at once if acetic acid is added, and is also accelerated by the addition of alcohol and ether. Acetic acid partially decomposes alkali tartrates if a mixture of the two is allowed to

evaporate, and conversely, a hydrogen tartrate partially decomposes an alkali acetate. The residue left after spontaneous evaporation is a mixture of normal tartrate, acetate, and hydrogen tartrate. A mixture of 1 mol. of tartaric acid and 2 mols. each of acetic acid and normal alkali tartrate, loses 95 per cent. of the acetic acid on spontaneous evaporation, and this is increased to 97 or 97.5 per cent. when the proportion of tartaric acid is doubled or trebled.

Calcium sulphate decomposes normal alkali tartrates completely, but hydrogen tartrates only incompletely, whether in presence of water or dilute alcohol. Its action on normal tartrates is not affected by the presence of potassium acetate, but its action on the hydrogen tartrates ceases to be limited in presence of the acetate.

Tartaric acid partially displaces sulphuric acid from potassium sulphate, and hydrochloric acid from potassium chloride, these acids being partially expelled when the solution is evaporated to dryness and heated. Under similar conditions, however, sodium chloride loses only a minute quantity of hydrochloric acid. C. H. B.

Easy Method of Preparing Lævorotatory Tartaric acid.

By WILHELM MARCKWALD (*Ber.*, 1896, **29**, 42—43).—A boiling aqueous solution of racemic acid is treated with half the cinchonine necessary to form the acid salt, and water is added until a clear solution is obtained, which is then allowed to cool; after remaining for a day, the cinchonine *l*-tartrate, which has crystallised out, is filtered off. The mother liquor deposits the *d*-tartrate, which is filtered off after two days; this second mother liquor is divided into two halves, and these are neutralised, the one with sodium hydroxide, the other with ammonia, filtered from precipitated cinchonine, mixed, and concentrated; sodium ammonium *d*-tartrate crystallises out on cooling, and this crystallisation is allowed to go on until the mother liquor has become inactive or feebly lævorotatory. The last mother liquor is worked up for racemic acid, which can be used over again, and the *d*- and *l*-tartrates obtained above are converted into the corresponding acids in the usual way. C. F. B.

Nitrocarbamide, Nitro-urethane, and Nitramide. By JOHANNES THIELE and ARTHUR LACHMAN (*Annalen*, 1895, **288**, 267—311; compare *Abstr.*, 1894, i, 399).—Nitrocarbamide is strongly acidic, liberating acetic acid from its salts. The *potassium* derivative is readily soluble in water, and the *silver* derivative crystallises in minute prisms dissolving readily in nitric acid and ammonia; the *mercury* derivative is very soluble in hydrochloric acid, dissolving with difficulty in nitric and sulphuric acids, and it yields nitrocarbamide when treated with ammonium sulphide.

Nitroethylcarbamide, $\text{NO}_2\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}\cdot\text{Et}$, is obtained by adding ethylic nitrate to a solution of ethylcarbamide in sulphuric acid; it crystallises from ether in long needles and melts at 130—131°. It dissolves readily in hot water, and is sparingly soluble in cold; hydrolysis with potash gives rise to ethylamine. The *ammonium* and *potassium* derivatives are hygroscopic; the *silver* derivative crystallises in white leaflets.

Nitro-urethane (*loc. cit.*) is prepared by treating a solution of urethane in sulphuric acid with ethylic nitrate at 0° ; it decomposes at 140° . The *potassium* derivative crystallises from water in large, rhombic prisms, and the *mercury* derivative is a white powder dissolving readily in hydrochloric acid; the *silver* derivative crystallises in aggregates of minute needles, and with methylic iodide yields nitromethylurethane (compare Abstr., 1895, i, 445).

Ethylic benzylidenehydrazinecarboxylate, $\text{CHPh}\cdot\text{N}\cdot\text{NH}\cdot\text{COOEt}$, is obtained by reducing nitro-urethane and agitating the product with benzaldehyde; it crystallises from dilute alcohol in long needles melting at $135\text{--}136^{\circ}$, and the *potassium* derivative is unstable in aqueous solution. The *hydrochloride* of ethylic hydrazinecarboxylate is obtained from the benzylidene derivative by the action of warm hydrochloric acid; it is readily soluble in water and alcohol, and separates in yellowish leaflets on adding ether to the solution in methylic alcohol.

The *mercury* derivative of nitramide (Abstr., 1894, ii, 412) is an unstable substance dissolving readily in hydrochloric, but only sparingly in nitric acid; the action of hot water gives rise to red mercuric oxide.

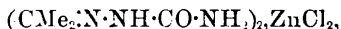
Nitrosocarbamide, $\text{NH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{NO}$, is obtained in solution when nitrocarbamide is reduced with zinc dust and caustic soda; the liquid develops an intense purple coloration with ferrous sulphate, and effervesces above 0° .

Nitroso-urethane, $\text{NO}\cdot\text{NH}\cdot\text{COOEt}$, is produced on reducing the ammonium derivative of nitro-urethane with zinc dust and acetic acid; it crystallises from petroleum in beautiful needles, and melts and decomposes completely at $51\text{--}52^{\circ}$, yielding aldehyde. It gives Liebermann's reaction, and does not develop a colour with ferrous sulphate and caustic soda; the aqueous solution effervesces vigorously when treated with acids or alkalis, yielding ethylic alcohol, carbonic anhydride, and nitrogen. The *silver* derivative is yellow, and explodes when heated; the *potassium* derivative crystallises in yellow needles, and the *ammonium* derivative in yellow leaflets. Potassium permanganate oxidises nitroso-urethane to nitro-urethane, and ammonia converts it into urethane, whilst aniline gives rise to phenyl-urethane.

Potassium nitrosocarbamate, $\text{NO}\cdot\text{NK}\cdot\text{COOK}$, is obtained from nitroso-urethane by the action of potash dissolved in methylic alcohol; it is a yellow powder, which explodes violently when brought in contact with water, but is perfectly stable in dry air. M. O. F.

Preparation of Semicarbazide. By JOHANNES THIELE and CARL HEUSER (*Annalen*, 1895, 288, 311—313).—The unstable character of nitrosocarbamide seriously diminishes the yield of semicarbazide obtained by the reduction of nitrocarbamide; under conditions which lead to the immediate reduction of nitrosocarbamide, however, 50 per cent. of the quantity required by theory may be obtained.

The zinc chloride compound of acetone-semicarbazone,

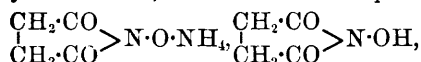


is obtained by adding sodium acetate and acetone to nitrosocarbamide reduced in acetic acid solution by means of zinc dust mixed with powdered ice; it crystallises from water in slender needles, and melts and decomposes at 196° . Ammonia converts the substance into acetonesemicarbazone, which may then be employed as a source of semicarbazide. M. O. F.

Cyanuric acid from Hydroxyoxamide. By HUGO SCHIFF and U. MONSACCHI (*Annalen*, 1895, **288**, 313—318, and *Gaz.*, **25**, ii, 446—450).—*Hydroxyloxamide*, $\text{OH}\cdot\text{NH}\cdot\text{CO}\cdot\text{CO}\cdot\text{NH}_2$, is obtained by the action of hydroxylamine on ethylic oxamate, and appears to be identical with oximamidoxalic acid, $\text{NH}_2\cdot\text{C}(\text{NOH})\cdot\text{COOH}$, described by Holleman (*Abstr.*, 1894, i, 571); the aqueous solution develops an intense red coloration with ferric chloride. *Acetoxylamide*, $\text{OAc}\cdot\text{NH}\cdot\text{CO}\cdot\text{CO}\cdot\text{NH}_2$, is obtained by the action of acetic anhydride on the foregoing compound, and crystallises in nacreous leaflets melting at $172\text{--}174^{\circ}$; the substance is indifferent towards ferric chloride, and, when heated at $100\text{--}110^{\circ}$ with acetic anhydride, gives rise to cyanuric acid, an intermediate compound, melting at 218° , being also formed.

Phenylhydroxyloxamide, $\text{OH}\cdot\text{NH}\cdot\text{CO}\cdot\text{CO}\cdot\text{NHPh}$, is formed when ethylic phenyloxamate is hydrolysed with alcoholic hydroxylamine, it crystallises in leaflets and melts at 159° . The *acetyl* derivative melts at $182\text{--}183^{\circ}$, and does not yield cyanuric acid. M. O. F.

Action of Hydroxylamine on Succinic Anhydride. By GIORGIO ERRERA (*Gazzetta*, 1895, ii, 25—37).—On adding succinic anhydride to an alcoholic solution of hydroxylamine, *hydroxylamine succinylhydroxamic acid* separates as a semi-solid mass. On mixing the anhydride with an alcoholic solution of hydroxylamine and sodium ethoxide, and adding ammonia and barium chloride, the *barium* salt, $(\text{C}_4\text{H}_6\text{NO}_4)_2\text{Ba}$, of succinylhydroxamic acid is obtained; it crystallises in small, colourless prisms, and gives a violet colour with ferric chloride; the *hydrogen barium* salt, $\text{C}_4\text{H}_5\text{NO}_2\text{Ba}\cdot 4\text{H}_2\text{O}$, crystallises in laminæ. *Succinylhydroxamic acid*, $\text{OH}\cdot\text{C}(\text{NOH})\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{COOH}$, can be obtained from these salts as a deliquescent, viscous liquid; on heating with acetic chloride, it yields *succinylacetoxylamine*, $\begin{smallmatrix} \text{CH}_2\cdot\text{CO} \\ \text{CH}_2\cdot\text{CO} \end{smallmatrix} > \text{N}\cdot\text{OAc}$, which separates from benzene in lustrous, colourless, orthorhombic crystals melting at $129\text{--}130^{\circ}$; $a:b:c = 0.99826:1:0.45945$. On crystallisation from hot water, it undergoes partial hydrolysis yielding a syrupy solution from which *succinylhydroxylamine* crystallises when the latter is evaporated over sulphuric acid. On adding alcoholic ammonia to the alcoholic solution of this amine or its acetyl derivative, an *ammonium* compound



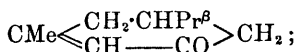
is deposited; it crystallises in colourless, monoclinic prisms, melts and decomposes at 175° , and is very soluble in water. On boiling with soda, it yields succinylhydroxamic acid. W. J. P.

The Hexamethylene Series. Synthesis of Nononaphthene.

By NICOLAI D. ZELINSKY and A. REFORMATZKY (*Ber.*, 1896, **29**, 214—216).—Trimethylhexamethylene alcohol, prepared synthetically from trimethylpimelic acid (this vol., i, 130), yields, when reduced, a saturated hydrocarbon, C_9H_{18} , which boils at $142-144^\circ$, has a sp. gr. = 0.7807 at $18^\circ/4^\circ$, and yields tribromopseudocumene when treated with bromine in the presence of aluminium bromide. This hydrocarbon, 1 : 2 : 5-trimethylhexamethylene, is thus nothing else than hexahydropseudocumene; it may be regarded as a synthetical nononaphthene. The nononaphthene, obtained from Caucasian naphtha by Markownikoff and Oglobin and by Konowaloff, is probably a mixture containing some hexahydropseudocumene; only 7 per cent. of it can be converted into tribromopseudocumene. C. F. B.

1 : 5-Diketones. By EMIL KNOEVENAGEL (*Annalen*, 1895, **288**, 321—360; compare Abstr., 1893, i, 419, and 1895, i, 48).—Ethylic isobutylidenediaceoacetate, $CHPr^s(CHAc \cdot COOEt)_2$, is obtained by adding diethylamine or piperidine (1 gram) to a mixture of ethylic acetoacetate (100 grams) and isobutylaldehyde (28 grams) cooled at 0° , four equal quantities of the base being subsequently added at intervals of 10 to 12 hours, while the temperature of the liquid is maintained between 0° and -10° ; it forms lustrous, colourless crystals, and melts at 117° .

Ethylic 3 : 5-methylisopropyl- Δ_2 -ketotetrahydrobenzene-4 : 6-dicarboxylate, $CMe \leq \begin{smallmatrix} CH(COOEt) \cdot CHPr^s \\ CH \text{ ————— } CO \end{smallmatrix} > CH \cdot COOEt$, is produced when acids and alkalis act on the foregoing substance; distillation gives rise to isomeric ethylic 3 : 5-methylisopropyl- Δ_2 -ketotetrahydrobenzenemonocarboxylates, the mixture forming a pale yellow oil, which boils at 170° under a pressure of 17 mm. (compare Hagemann, Abstr., 1893, i, 393). *Ethylic 3 : 5-methylisopropyl- Δ_2 -ketotetrahydrobenzene-4-carboxylate* is isolated from this mixture by means of its insolubility in caustic soda; it boils at 161° and 170° under pressures of 11 mm. and 17 mm. respectively, and the alcoholic solution is indifferent towards ferric chloride. *Ethylic 3 : 5-methylisopropyl- Δ_2 -ketotetrahydrobenzene-6-carboxylate* is soluble in caustic soda; it boils at 166° and 170° under pressures of 14 mm. and 17 mm. respectively, and develops an intense reddish-violet coloration with ferric chloride. Hydrolysis of these two ethylic salts converts them into the corresponding acids, which spontaneously lose carbonic anhydride, yielding 3 : 5-methylisopropyl- Δ_2 -ketotetrahydrobenzene, or metacamphor,



this substance is also formed when ethylic isobutylidenediaceoacetate is heated for two hours at 110° (compare Abstr., 1893, i, 419, and 1894, i, 575).

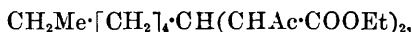
Ethylic isovalerylidenediaceoacetate, $CH_2Pr^s \cdot CH(CHAc \cdot COOEt)_2$, is obtained from ethylic acetoacetate and isovaleraldehyde by means of piperidine or diethylamine; it crystallises from dilute alcohol, and melts at $134-135^\circ$. When heated with water for five hours in a

reflux apparatus, it yields *ethylic 3 : 5-methylisobutyl- Δ_2 -ketotetrahydrobenzene-4 : 6-dicarboxylate*, a colourless liquid, which boils at 186—188° under a pressure of 20 mm.; the *oxime* crystallises in small, white needles, which melt at 108—109°, and yields a *benzoyl* derivative, crystallising from dilute alcohol in leaflets, and melting at 157—158°. When *ethylic 3 : 5-methylisobutyl- Δ_2 -ketotetrahydrobenzene-4 : 6-dicarboxylate* is hydrolysed with 20 per cent. sulphuric acid, a mixture of ethylic salts is obtained, boiling at 167—169° under a pressure of 20 mm., and these are separated by the method adopted for the isopropylic derivatives. *Ethylic 3 : 5-methylisobutyl- Δ_2 -ketotetrahydrobenzene-6-carboxylate* forms a *phenylhydrazone*, which crystallises from alcohol in small, white needles, and melts at 162—163°. *Ethylic 3 : 5-methylisobutyl- Δ_2 -ketotetrahydrobenzene-4-carboxylate* yields an *oxime*, which melts at 101—103°, and gives rise to a *benzoyl* derivative melting at 146—148°.

3 : 5-Methylisobutyl- Δ_2 -ketotetrahydrobenzene is produced when *ethylic isovalerylidenediaceoacetate* is heated with alcoholic potash for 2—3 hours, and it is also obtained by hydrolysing the foregoing ethylic mono- and di-carboxylates; the ketone has an agreeable odour, and boils at 146—145° and 130° under pressures of 22 mm. and 10 mm. respectively. The *oxime* crystallises in colourless needles, melting at 92—94°, and gives rise to a *benzoyl* derivative, which crystallises in lustrous leaflets, and melts at 138—140°. The *phenylhydrazone* crystallises from alcohol in silky needles, and melts at 149—151°.

3 : 5-Methylisobutylphenol is obtained by adding bromine to a solution of the ketone in carbon bisulphide, and, after removing the solvent, heating the product at 120°; it boils at 142—144° under a pressure of 20 mm., and is indifferent towards ferric chloride. The *tribromo-derivative*, $C_{11}H_{13}OBr_3$, crystallises in white needles, and melts at 128—130°.

Ethylic oenanthyldenediacetoacetate,



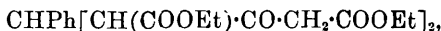
crystallises from petroleum in white, lustrous needles, and melts at 71°; it is readily converted into *ethylic 3 : 5-methylhexyl- Δ_2 -ketotetrahydrobenzene-4 : 6-dicarboxylate*, which boils at 195—196° and 202—204° under pressures of 9 mm. and 17 mm. respectively. The *oxime* of the latter ethylic salt is produced when hydroxylamine acts on the former; it melts at 116—118°, and yields a *benzoyl* derivative, which crystallises in colourless, lustrous leaflets, and melts at 165—166°.

Ethylic 3 : 5-methylhexyl- Δ_2 -ketotetrahydrobenzene-4-carboxylate is separated by means of its insolubility in caustic soda from the mixture of isomerides obtained on hydrolysing the foregoing ethylic dicarboxylates; it is indifferent towards ferric chloride, and yields an *oxime* melting at 109—111°, which gives rise to a *benzoyl* derivative, melting at 157—159°. *Ethylic 3 : 5-methylhexyl- Δ_2 -ketotetrahydrobenzene-6-carboxylate* is also separated from the mixture, which boils at 186—188° under a pressure of 18 mm.; it develops a dark violet coloration with ferric chloride, and yields a *phenylhydrazone*, which crystallises in orange-yellow needles, and melts at 146—147°.

3:5-Methylhexyl- Δ_2 -ketotetrahydrobenzene is the final product arising from hydrolysis of the foregoing ethylic salts; it has a bitter taste and agreeable odour, and boils at 166—168° under a pressure of 22 mm. The *oxime* melts at 103—105°, and yields a *benzoyl* derivative, which crystallises in white, lustrous leaflets, and melts at 150—152°. The *phenylhydrazone* crystallises in silky needles, and melts at 157—159°.

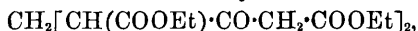
3:5-Methylhexylphenol boils at 160—162° under a pressure of 18 mm., and is indifferent towards ferric chloride; the *tribromo*-derivative, $C_{13}H_{17}OBr_3$, melts at 137—139°

Ethylic benzylidenebisacetonedicarboxylate,



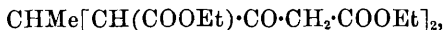
is obtained by the action of benzaldehyde on ethylic acetonedicarboxylate, employing diethylamine, piperidine, or ammonia as the condensing agent; it crystallises from alcohol in white, silky needles, and melts at 146°. Although water is eliminated very readily, an individual ketotetrahydrobenzene derivative has not been isolated by distillation; successive treatment with sodium ethoxide and aqueous potash, however, converts it into 3:5-methylphenyl- Δ_2 -ketotetrahydrobenzene (Abstr., 1895, i, 50).

Ethylic methylidenebisacetonedicarboxylate,



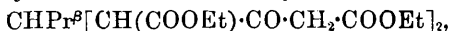
is prepared from formaldehyde and ethylic acetonedicarboxylate, diethylamine being used as the condensing agent; it melts at 105°. Hydrolysis converts it into 3-methyl- Δ_2 -ketotetrahydrobenzene, identical with the substance obtained on hydrolysing ethylic 3-methyl- Δ_2 -ketotetrahydrobenzene-4:6-dicarboxylate (*loc. cit.*).

Ethylic ethylidenebisacetonedicarboxylate,



obtained from acetaldehyde, ethylic acetonedicarboxylate, and diethylamine, crystallises in white, silky needles, and melts at 115°; hydrolysis with 20 per cent. sulphuric acid converts it into 3:5-dimethyl- Δ_2 -ketotetrahydrobenzene.

Ethylic isobutylidenebisacetonedicarboxylate,



melts at 104°; on hydrolysis, it yields 3:5-methylisopropyl- Δ_2 -ketotetrahydrobenzene. *Ethylic isovalerylidenebisacetonedicarboxylate* melts at 118°, and yields 3:5-methylisobutyl- Δ_2 -ketotetrahydrobenzene when hydrolysed. *Ethylic oenanthylidenebisacetonedicarboxylate* melts at 125°, and yields 3:5-methylhexyl- Δ_2 -ketotetrahydrobenzene on hydrolysis.

M. O. F.

Derivatives of Chlorodihydrobenzene. By CH. GUNDLICH and EMIL KNOEVENAGEL (*Ber.*, 1896, **29**, 169—171; compare Abstr., 1895, i, 86 and 654).—When 1:3-methylisopropylcyclohexanone (3:5-methylisopropyl- Δ_2 -ketotetrahydrobenzene) is treated in chloroform solution with phosphorus pentachloride, hydrogen chloride is given off, and 5-chlorodihydrometacymene (1:3:5-methylisopropylchlorocyclohexadiene) is formed. This distils over at 106° under a pressure of 15 mm.

as a colourless, limpid oil; it is transformed back into the ketone by the action of 95 per cent. sulphuric acid. On treatment with bromine and quinoline, it yields 5-chlorometacymene, which distils under atmospheric pressure at 222—223°.

5 : 2 : 4 : 6-Chlorotrinitrometacymene, obtained by the action of nitric acid on the preceding compound, forms colourless crystals, melts at 124—125°, sublimes on heating, and smells intensely of musk.

The trinitro-compound, with aniline, yields 2 : 4 : 6 : 5-trinitroanilidometacymene, which melts at 155°; whilst with alcoholic ammonia it yields 2 : 4 : 6-trinitro-1 : 3 : 5-cymidine, which melts at 103—104°.

5-Chlorodihydrometaisobutyltoluene (1 : 3 : 5-methylisobutylchlorocyclohexadiene) is obtained by the action of phosphorus pentachloride on methylisobutylcyclohexanon (*Annalen*, 288, 336). It is a strongly refractive liquid, and distils at 113—115° under a pressure of 15 mm. When treated with bromine or quinoline, it yields 5-chlorometaisobutyltoluene, which distils under atmospheric pressure at 234—235°.

5-Chlorometahexyldihydrotoluene (1 : 3 : 5-methylhexylchlorocyclohexadiene) boils at 148—150° under a pressure of 25 mm., and with bromine and quinoline yields 5-chlorometahexyltoluene, which distils under atmospheric pressure at 273—275°. J. J. S.

The Benzene Problem. By VICTOR MEYER (*Ber.*, 1895, 3195—3196).—This is a reply to criticisms by Brühl (this vol., i, 147) on the paper by Heyl and V. Meyer (*ibid.*, 145). As regards the question of priority between Brühl and Wegscheider (*Abstr.*, 1895, i, 593, and 449) concerning the hydrolysis of ethereal salts, the author points out that Conrad and Brückner were the first to draw attention to the rules regulating the hydrolysis, and to compare the results of hydrolysis with those of etherification. J. J. S.

The Benzene Nucleus. By WILHELM VAUBEL (*J. pr. Chem.*, 1895, [2], 52, 548—555).—The author shows that his configuration for benzene (*Abstr.*, 1894, i, 325) is in accord with the following facts. (1) Metanitriline hydrochloride is the most stable of the nitriline hydrochlorides (Lellmann, *Abstr.*, 1885, 251). (2) Ammonia reacts with ortho- and para-bromonitrobenzene to form nitrilines, but not with metabromonitrobenzene (Schöpf, *Abstr.*, 1892, 335; P. Fischer, *ibid.*, 331; Lobry de Bruyn, *Abstr.*, 1891, 428). (3) Ortho- and para-nitriline react with ammonia to form the corresponding nitrophenols; metanitriline does not so react. (4) Ammonia reacts with ortho- and para-nitransoil to form the corresponding nitrilines, but not with metanitransoil. (5) Of the nitrilines the meta-compound combines most readily with phenylthiocarbimide. (6) Ortho- and para-xylene are readily oxidised to the corresponding toluic acids, metaxylene far less readily. (7) Hydrochloric acid at high temperatures converts ortho- and para-hydroxybenzoic acids into phenol, but not the meta-acid. (8) Of the nitrobenzaldehydes, the meta-compound is more easily oxidised by nitric acid than is the ortho-compound. (9) Metahydroxybenzoic acid is reduced to the corresponding alcohol by sodium amalgam, in which respect it differs from both its isomerides.

In the same connection, the author quotes Sudborough on the

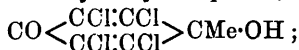
substituted benzoic chlorides and the hydrolysis of nitriles and amides (Trans, 1895, 587, 601). Some speculations concerning the manner in which naphthalene tetrachloride yields four dichloronaphthalenes according to the treatment to which it is subjected, conclude the paper.

A. G. B.

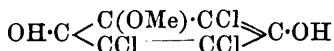
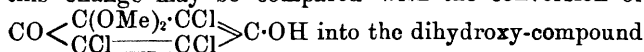
4 : 3 : 5-Bromodinitrotoluene and its Derivatives. By C. LORING JACKSON and M. H. ITNER (*Ber.*, 1895, 28, 3063—3066).—This substance was prepared by the diazo-reaction from the corresponding 4-amido-compound; it forms yellowish prisms, and melts at 118°; with aniline it yields, in the cold, 3 : 5 : 4-dinitranilidotoluene, which is orange-yellow and melts at 169°. The bromo-compound does not react with ethylic sodiomalonate, and is oxidised only with difficulty, dichromate and sulphuric acid converting it into 4 : 3 : 5-bromodinitrobenzoic acid. This forms colourless plates, and melts at 181°; the bromine atom in it is much more easily replaced than in the case of the preceding compound; on warming with ammonia, it is converted into the 4-amido-compound (chrysanisic acid); with aniline, it yields the orange-yellow 3 : 5 : 4-dinitroanilidobenzoic acid melting at 236°, and with ethylic sodiomalonate, it gives ethylic 2 : 6 : 4-dinitro-carboxyphenylmalonate, $\text{COOH} \cdot \text{C}_6\text{H}_2(\text{NO}_2)_2 \cdot \text{CH}(\text{COOEt})_2$, which melts at 176°. With most of these substances sodium ethoxide forms unstable coloured substances, possibly adding itself on to the nitro-groups; certainly the other groups are not displaced.

C. F. B.

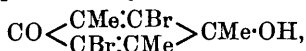
New Series of Quinonoid Derivatives. By THEODOR ZINCKE (*Ber.*, 1895, 28, 3121—3127).—When tetrachloroparacresol is oxidised with nitric acid, a single atom of oxygen is taken up, giving rise to the formation of the hydroxy-compound,



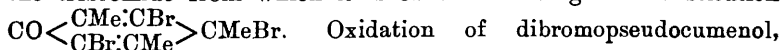
this change may be compared with the conversion of the ketone



(Abstr., 1894, i, 232). It is probable that hydroxydibromopseudocumenol (Auwers, this vol., i, 151) is a member of the new class of derivatives, being represented by the formula



the tribromide from which it is obtained having the constitution



Oxidation of dibromopseudocumenol, however, yields a hydroxy-derivative which is isomeric and not identical with the compound described by Auwers.

M. O. F.

Preparation of Trichlorotoluquinone. By KARL ELBS and E. BRUNNSCHWEILER (*J. pr. Chem.*, 1895, [2], 52, 559—560).—20 grams of orthotoluidine is dissolved in the necessary quantity of dilute

hydrochloric acid, and 700 c.c. of crude concentrated hydrochloric acid is added, and, in the course of an hour, 190 grams of dry, powdered sodium dichromate are added. The temperature is kept below 30—40°, and, after two hours, the mixture is heated for half an hour on the water bath, then diluted with a litre of water and filtered. The contents of the filter are washed into a flask with a little strong hydrochloric acid, and heated for an hour on the water bath; water is again added, the whole is filtered, and the solid once more washed with dilute hydrochloric acid into the flask. Several grams of dichromate are now added, and, after warming for a quarter of an hour, the solid matter is filtered and washed. After two treatments with alcohol, the residual dirty yellow powder is crystallised from benzene. In this way, 20 grams of toluidine yield 16—17 grams of trichlorotoluquinone. Aniline may be similarly converted into chloranil.

A. G. B.

Synthesis and Constitution of Eugenol. By CHARLES MOUREAU (*Compt. rend.*, 1895, **121**, 721—723).—The action of allylic iodide on dimethylcatechol (veratrol), $C_6H_4(OMe)_2$, yields methyleugenol identical in physical and chemical properties with the natural product. Some methylic iodide, catechol, and guaiacol are formed at the same time. The methyleugenol, when boiled with alcoholic potash, is converted into isomethyleugenol; with chromic mixture, it yields methylvanillin and methylvanillic acid, and with potassium permanganate, it yields the same acid [$COOH : OMe : OH = 1 : 3 : 4$]. These results confirm the constitution generally ascribed to eugenol.

C. H. B.

Orthonitrobenzylic Mercaptan. By SIEGMUND GABRIEL and ROB. STELZNER (*Ber.*, 1896, **29**, 160—165; compare *Abstr.*, 1895, 432).—Orthonitrobenzylic carbaminthiolate,



when boiled with 10 times its weight of 20 per cent. hydrochloric acid, yields *orthonitrobenzylic hydrosulphide*, $NO_2 \cdot C_6H_4 \cdot CH_2 \cdot SH$, together with a small quantity of orthonitrobenzylic sulphide; the former may be separated by steam distillation, as it is readily volatile. By exposing a concentrated solution of the mercaptan in methylic alcohol to low temperatures, it is obtained in long, yellow needles, which have a characteristic odour, and melt at 42—44°. The author thinks that his compound is identical with Jahoda's nitrobenzylic bisulphide (m. p. 47°) (*Abstr.*, 1890, 487), since the true bisulphide, according to Cassirer (*Abstr.*, 1893, 16), melts at 112—113°. This bisulphide may easily be obtained from the hydrosulphide by treatment with a solution of iodine. The hydrosulphide, when treated with a 33 per cent. solution of potassium hydroxide, yields phenoisothiazole and nitrobenzylic bisulphide; zinc chloride also gives the same thiazole.

Methylic orthonitrobenzylic sulphide, $NO_2 \cdot C_6H_4 \cdot CH_2 \cdot SMe$, is obtained by dissolving the hydrosulphide in methylic alcohol, and treating the mixture with sodium methoxide and methylic iodide; it is a thick, yellowish oil, and, on heating it with methylic iodide at 100°, is

decomposed, yielding nitrobenzylic iodide, trimethylsulphine iodide, and a third substance which melts at $67-70^{\circ}$.

Methylic orthoamidobenzylic sulphide, obtained by the action of zinc dust and acetic acid on the nitro-compound, is a colourless oil, which boils at $277-278^{\circ}$, and does not solidify at -18° . The *hydrochloride* crystallises in long, colourless needles; its acetyl derivative, $\text{NHAc}\cdot\text{C}_6\text{H}_4\cdot\text{SMe}$, melts at 102° , and its benzoyl derivative at 118° .

J. J. S.

Action of Hypobromous acid and Hypochlorous acid on Acid Anilides. By E. E. SLOSSON (*Ber.*, 1895, 28, 3265—3270).—*Acetobromamidobenzene*, NBrPhAc , mixed with acetoparabromanilide, is obtained by the action of alkaline hypobromite solution on acetanilide at 0° ; the liquid is acidified with boric acid, when the compound is deposited in rectangular, yellowish plates, melting at $75-80^{\circ}$. It is unstable, and in presence of moisture is converted into acetoparabromanilide; the change is instantaneous at its melting point or when it is boiled with water; it liberates iodine from potassium iodide and nitrogen from ammonia, and in stability is midway between the corresponding chloro- and iodo-derivatives. *Formobromamidobenzene*, $\text{HCO}\cdot\text{NPhBr}$, resembles the preceding compound in general properties, and is formed in a similar manner from formanilide; it is deposited in yellow crystals melting at $55-57^{\circ}$. The above preparations contained about 10 and 20 per cent. respectively of the parabromanilides. Sodium hypochlorite gives a better yield of acetochloramidobenzene than bleaching powder and hydrochloric acid; it was therefore employed in the preparation of the compounds described below. *Formochloramidobenzene*,



crystallises from ether or dilute acetic acid in colourless plates, melts at $43-44^{\circ}$, is not reduced to formanilide by the action of ammonia, hydriodic acid, or alcohol, and is not changed when heated alone at 100° . *Formoparachloranilide*, $\text{HCO}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\text{Cl}$, is prepared by heating the preceding compound with hydrochloric acid, or from parachloraniline and formic acid, and is deposited in colourless crystals melting at 101° . *Benzochloramidobenzene*, NCIPhBz , crystallises from light petroleum in needles melting at $78-80^{\circ}$.

The action of an alkali does not cause intramolecular rearrangement (exchange of position between the haloïd and radicle; Beckmann's reaction) in any of the above haloïd amides, although compounds of the analogous type $\text{RCO}\cdot\text{NHX}$ ($\text{X} = \text{Cl}$ or Br) react in this manner with the greatest readiness; the cause of this difference in behaviour is being investigated.

J. B. T.

Thioaldolaniline and Aldehyde-green. By WILHELM VON MILLER and JOSEF PLÖCHL (*Ber.*, 1896, 29, 59—61).—Recognising that substances containing the group $>\text{C:N}$ readily form additive products, the authors thought it possible that this group might directly take up hydrogen sulphide or sulphur. As a matter of fact, aldolanilide, $\text{OH}\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{CH:NPh}$ (*Abstr.*, 1894, i, 414), could not be made to unite simply with hydrogen sulphide; but, by heating it in absolute alcoholic solution with crystallised ammonium sulphide,

a white substance, $\text{OH} \cdot \text{CHMe} \cdot \text{CH}_2 \cdot \text{CH} < \begin{smallmatrix} \text{NPh} \\ | \\ \text{S} \end{smallmatrix}$, was obtained; this melts at 92° , and turns yellowish when kept for a time. The sulphur in aldehyde-green doubtless exists therein combined in much the same fashion. C. F. B.

Thiodiazo-derivatives. By ARTHUR R. HANTZSCH and HANS FREESE (*Ber.*, 1895, **28**, 3237—3251).—The thiodiazo-derivatives described below were all prepared by the action of phenylic hydrosulphide on diazonium salts in alkaline solution. The diazo-ethers, $\text{RN} \cdot \text{NOR}$, are now generally recognised as iso-derivatives, and these are probably “anti” compounds, but as all efforts to prepare “syn” isomerides have been unsuccessful, this is not absolutely proved. The thio-ethers are more stable than the oxy-ethers, and do not combine with naphthols either in alkaline or alcoholic solution; they are also probably “anti” compounds, but attempts to prepare isomerides were unsuccessful. The slow combination of naphthol and diazosulphanilic acid thio-ether is probably caused by the regeneration, under the influence of water, of some diazosulphanilic acid. The diazo-ethers are yellow and stable at 0° ; alkalis and dilute acids are without action on them; with concentrated acids, their components are regenerated; they form unstable additive products with hydrogen chloride, and, when heated, explode and yield nitrogen; when warmed with water, nitrogen and a sulphide, RSPH , are formed, but hydrolysis also occurs, and consequently a phenol and phenylic hydrosulphide, or its oxidation product, phenylic bisulphide, are also produced.

Diazobenzenethiophenyl ether, $\text{PhN} \cdot \text{N} \cdot \text{SPh}$, prepared from phenylic hydrosulphide and diazonium chloride at -5° , is oily and unstable. *Antiparachlorodiazobenzenethiophenyl ether*, $\text{C}_6\text{H}_4\text{Cl} \cdot \text{N} \cdot \text{N} \cdot \text{SPh}$, prepared from parachlorodiazonium chloride and phenylic hydrosulphide, crystallises from ether at 0° in yellow, rectangular plates melting at 60 — 62° ; the yield is 84 per cent. of the theoretical. The ether, unlike the oxygen derivative, is only very slowly attacked by glacial acetic acid, and the product does not combine with β -naphthol; it is readily soluble in presence of sodium methoxide, but at low temperatures undergoes no further change. When heated with alcohol, nitrogen, parachlorophenylic sulphide, and phenylic bisulphide are formed. During the preparation of the ether, a highly unstable compound, possibly the “syn” derivative, is formed if the liquid is cooled so that a portion freezes; it evolves nitrogen below 0° , and on one occasion exploded at this temperature while still moist. *Parabromodiazobenzenethiophenyl ether*, $\text{C}_6\text{H}_4\text{Br} \cdot \text{N} \cdot \text{N} \cdot \text{SPh}$, from parabromodiazonium chloride, crystallises in dark, reddish-brown plates, melts at 44° , and is less stable than the chloro-derivative; the yield is about 30 per cent. of the theoretical. *Pariododiazobenzenethiophenyl ether* is even less stable than the bromo-derivative, and is prepared in a similar manner. *Orthochlorodiazobenzenethiophenyl ether*, evolves no nitrogen during its preparation; like the preceding compound, it is oily. *Dichlorodiazobenzenethiophenyl ether*, $\text{C}_6\text{H}_3\text{Cl}_2 \cdot \text{N} \cdot \text{N} \cdot \text{SPh}$ [$\text{N} : \text{Cl} : \text{Cl} = 1 : 2 : 4$], crystallises in golden plates, and melts at 55 — 56° . The corresponding dibromo- and diiodo-derivatives and tribromodiazobenzenethiophenyl

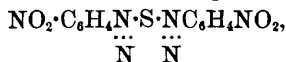
ether, $C_6H_2Br_3N:N\cdot N\cdot SPh$ [$Br_3 = 2:4:6$], are difficult to purify, and apparently are liquid at 0° .

Antiparanitrodiazobenzenethiophenyl ether, $NO_2\cdot C_6H_4\cdot N:N\cdot SPh$, crystallises from warm alcohol in golden plates, melts at $96-97^\circ$, and is the most stable compound of this class hitherto prepared; as the oxy-ether is similarly characterised, the nitro-group appears to be specially favourable to the production of compounds possessing the anti-configuration. Antinitrodiazobenzene hydroxide does not react with phenylic hydrosulphide, but the sodium salt (sodium nitrophenyl-nitrosamine) yields the diazo-thio-ether and sodium hydroxide when treated with phenylic hydrosulphide in alcoholic solution. Paranitrobenzenediazonium perbromide is formed by the action of bromine on the thio-ether; with iodine, paranitroiodobenzene is probably formed, whilst iodine chloride yields a compound which melts at $150-156^\circ$, and is possibly nitrochloriodobenzene.

Syn-sodium diazosulphanilate thiophenyl ether, $SO_3Na\cdot C_6H_4\cdot N:N\cdot SPh$, is readily prepared by the interaction of phenylic hydrosulphide and diazosulphanilic acid in alkaline solution at 0° , but unless alkali is present in considerable excess the reaction proceeds slowly; it crystallises in yellow plates, and, when dry, is stable at the ordinary temperature, and in aqueous solution at 0° ; the yield is about 80 per cent. of the theoretical. The *silver salt* is dark brown, and, like the sodium salt, immediately decomposes into its constituents when acidified with hydrochloric acid. The "anti" sodium salt does not react with phenylic hydrosulphide. The diazophenols combine with phenylic hydrosulphide in neutral, alkaline, and acid solution, but the products were not investigated on account of their great instability. When the free diazophenols, prepared by the action of silver oxide on the hydrochlorides, are treated at 0° with hydrogen sulphide, compounds are formed which probably are additive products of hydrogen sulphide and diazophenol hydrosulphide, $OH\cdot C_6H_4\cdot N:N\cdot SH, H_2S$. The *para*-compound crystallises in deep red, microscopic needles, melts and decomposes at $74-75^\circ$, is unstable above 0° , and decomposes in contact with indifferent solvents, such as chloroform, light petroleum, and particularly ether, into sulphur, nitrogen, hydrogen sulphide, and probably phenol. The *ortho*-derivative resembles the preceding compound, melts at $69-70^\circ$, and may be purified by dissolving it in cold glacial acetic acid and precipitating with ice-cold water.

J. B. T.

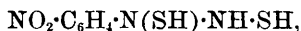
Thiodiazo-derivatives. By EUGEN BAMBERGER and E. KRAUS (*Ber.*, 1896, **29**, 272-286; compare Hantzsch and Freese, preceding Abstr.).—*Diparanitrodiazobenzene sulphide*,



is prepared by the action of hydrogen sulphide at 0° , on aqueous paranitrodiazobenzene chloride solution which has been almost neutralised with soda; the product is treated with ammonia to remove any diazomercaptan hydrosulphide (see below); it crystallizes from acetone, on the addition of ice-cold water, in sulphur-yellow, lustrous needles, which explode at 89° , and also when pressed,

or when treated with concentrated sulphuric acid or nitric acid vapour; and, on one occasion, when it was gently heated on the water bath while covered with a large amount of light petroleum. It is insoluble in alkali at the ordinary temperature, and when heated, decomposes; concentrated alcoholic potash decomposes it at the ordinary temperature; in acetone solution, it gives a violet-red coloration with soda, probably caused by the formation of a formazyl-derivative. Lead acetate added to the diazosulphide in alcoholic solution gives lead sulphide; it combines instantaneously with α -naphthol when warmed more slowly at the ordinary temperature, giving an orange-yellow coloration changing to violet with alkali; with α -naphthylamine the sulphide, in acetic acid solution, gives immediately a violet coloration, and it also combines directly with alkaline β -naphthol. With resorcinol, a characteristic violet-red coloration is produced. Benzene reacts at the ordinary temperature with the diazo-sulphide forming paranitrodiphenyl, paradinitrophenylic bisulphide, sulphur, and nitrogen; the reaction takes place in two stages, nitrodiphenyl, nitrogen, and hydrogen sulphide are first formed, and the latter converts a portion of the diazo-sulphide into dinitrophenyl-bisulphide. Toluene and pyridine react like benzene, paranitrophenyltolyl and paranitrophenylpyridine, respectively, being produced, together with dinitrophenylic bisulphide and sulphur.

Paranitrodiazobenzene mercaptanhydrosulphide,



is prepared by the action of hydrogen sulphide at 0° on aqueous paranitrodiazobenzene chloride solution, in presence of hydrogen chloride in excess; it is purified by dissolving it in ammonia and continuously adding the solution to well cooled acetic acid, the precipitate is then crystallised from light petroleum, or from acetone by the addition of ice-cold water. It forms red, metallic, lustrous needles with a blue reflex, melts at 86° , is decomposed when heated with alcohol or acetone, readily dissolves in alkalis and ammonia, and is reprecipitated by acids. It does not combine with phenols in presence of either alkali or acid. The molecular weight was determined by the cryoscopic method; the yield is about 50 per cent. of the nitraniline employed. The *lead* salt is pale red, but becomes brown with a bronze lustre when dry; the *silver* salt is brownish-red and soon blackens; the *mercuric* salt, $\text{Hg}(\text{N} \leftarrow \text{S} \text{---} \text{N}(\text{C}_6\text{H}_4 \cdot \text{NO}_2) \text{---} \text{S} \rightarrow \text{Hg})_2$, is pale orange-yellow and crystalline.

When heated, the mercaptan hydrosulphide solidifies immediately after melting, the solid then consisting of paranitraniline, paranitrophenylhydrazine, dinitrophenylic bisulphide, and sulphur, whilst hydrogen sulphide, nitrogen, and, in small quantity, nitrobenzene are evolved. The same result is obtained by boiling the mercaptan hydrosulphide for a considerable time with light petroleum or alcohol. The first stage in this decomposition probably consists in a resolution of the mercaptan hydrosulphide into nitrodiazobenzene mercaptan and hydrogen sulphide, the latter then reduces a portion of the former to nitrophenylhydrazine, nitraniline, and sulphur, whilst the remainder of the mercaptan is oxidised by the air to nitrogen and dinitrophenylic bisulphide; the

last compound is formed by the action of air on the mercaptan hydrosulphide in ammoniacal solution, and also by the action of iodine; it melts at 180.5° , and not at $168-173^{\circ}$ as stated by Leuckart. Benzene and toluene react with the mercaptan hydrosulphide like alcohol, but in addition, nitrodiphenyl and nitrophenyltolyl respectively, are formed.

Diparanitrodiazobenzene bisulphide, $S_2(N \cdot N \cdot C_6H_4 \cdot NO_2)_2$, is prepared like the above mercaptan hydrosulphide, except that the treatment with hydrogen sulphide is prolonged, the hydrosulphide is removed from the product by treating it with ammonia, and the residue is extracted at 0° with acetone in which the bisulphide dissolves more readily than the monosulphide. It is purified in a similar manner to the latter, crystallises in lustrous, pale sulphur-yellow needles or plates, melts and decomposes at $120-123^{\circ}$, does not explode, and is stable at the ordinary temperature, but decomposes when heated with acetone, alcohol, or benzene. The bisulphide dissolves in alkali only when boiled, gas is evolved and the solution becomes reddish-brown; in alcoholic or acetone solution, it gives a claret coloration with alkali; with α -naphthylamine, a violet-red coloration is slowly produced; with α -naphthol and alkali, a dark brownish-red coloration is obtained which changes slowly to violet. With resorcinol, the mono- and bisulphides react almost identically, whilst with benzene, the bisulphide yields the same products as the monosulphide, but the action proceeds less readily. Isoparanitrodiazobenzene hydroxide, with hydrogen sulphide, yields, at $-10^{\circ}-0^{\circ}$, paratraniline and paranitrophenylhydrazine. Dinitrodiazobenzene sulphide, in presence of sulphuric acid, is converted by the action of hydrogen sulphide into the bisulphide, and the mercaptan hydrosulphide; this confirms the authors' view that, with nitrodiazobenzene, the hydrogen sulphide first yields the monosulphide, a part of the latter being then converted into bisulphide, and part into the hydrosulphide. As yet the preceding formulæ can only be regarded as provisional.

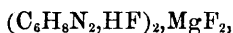
J. B. T.

Salts of Phenylhydrazine and of α -Methylphenylhydrazine.

By SIRO GRIMALDI (*Real. Accad. Lincei*, 1893, i, 483-491).—*Phenylhydrazine hydriodide*, $NHPh \cdot NH_2 \cdot HI$, crystallises in white scales or needles melting at $120-122^{\circ}$, and is readily soluble in water, alcohol, or acetone, giving neutral solutions; its solubility in water is increased by the addition of alkali iodides. With potassium iodide and magnesium iodide, it yields double salts of the compositions $C_6H_5N_2 \cdot HI \cdot KI$, and $(C_6H_5N_2 \cdot HI)_2 \cdot MgI_2$. The *hydrofluoride*,



crystallises in lustrous, white laminae, and is soluble in water or alcohol; its solubility in water is increased by adding alkali fluorides and its aqueous solution is neutral to test papers. It can be easily sublimed unchanged, and forms double salts of the compositions $C_6H_5N_2 \cdot HF \cdot KF$; $C_6H_5N_2 \cdot HF \cdot NaF$; $C_6H_5N_2 \cdot HF \cdot LiF$, and



which crystallise in white laminae and are very soluble in water.

α-Methylphenylhydrazine hydrofluoride, $\text{NMePh}\cdot\text{NH}_2\cdot\text{HF}$, crystallises in colourless laminæ, and is very soluble in water.

W. J. P.

Constitution of Dicyanophenylhydrazine and Bladin's Triazole Compounds. By AMERICO ANDREOCCI (*Real. Accad. Lincei*, 1893, ii, 302—310).—The author replies to Bamberger and de Gruyter's criticisms (Abstr., 1894, i, 23) of his previous work (Abstr., 1892, 636).

W. J. P.

Migration of the Diazo-Group. By C. SCHRAUBE and M. FRITSCH (*Ber.*, 1896, 29, 287—294).—Diazosulphanilic acid and paratoluidine hydrochloride at 0° yield sulphanilic acid and diazotoluene chloride, as Griess has previously shown; the course of the reaction may be followed by means of alkaline β -naphthol solution, with which the diazotoluene forms an insoluble compound; it is complete after 24 hours, but the presence of hydrochloric acid in large excess completely prevents the change. In neutral solution, the above compounds immediately yield the diazoamido-derivative, $\text{C}_6\text{H}_4\text{Me}\cdot\text{N}:\text{N}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_3\text{H}$, in the form of a yellow *toluidine* salt; the *sodium* salt crystallises in long, thin, pale-yellow plates; the *disodium* salt is deep yellow; the *calcium* salt is pale yellow, and crystalline; the *barium* salt is sparingly soluble. When treated with acids, the sodium salt yields sulphanilic acid and diazotoluene chloride. In alkaline solution, diazosulphanilic acid and paratoluidine yield a diazoamido-derivative of sulphanilic acid and diazoamidotoluene, the *barium* salt, $\text{N}\begin{smallmatrix} \text{N}-\text{C}_6\text{H}_4\cdot\text{SO}_3 \\ \text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_3 \end{smallmatrix} > \text{Ba}$, of the former, being crystalline. With less alkali, the mixed diazoamido-compound (see above) is also formed. Diazotoluene chloride and sulphanilic acid are without action in presence of mineral acids, but, with sodium sulphanilate, the reaction is normal, whilst the two sodium salts yield the two diazoamido-compounds. Paranitrodiazobenzene chloride and paratoluidine readily yield a diazoamido-derivative in acid solution, but in presence of a large excess of acid, the diazo-group migrates and the reaction may be readily followed by testing portions of the liquid with α -naphthylamine hydrochloride in hydrochloric acid solution. In neutral or faintly acid solution, the diazoamido-derivative is formed, and is quickly resolved by hydrochloric acid into paradiazotoluene and paranitraniline. The migration of the diazo-group resembles the formation of diazoamido-derivatives, as in both cases the imido-group combines with the most negative radicle, and the diazo-group with the positive one. Following V. Meyer, the interaction of diazosulphanilic acid and paratoluidine in alkaline solution is regarded as taking place in several stages, an additive compound, $\text{C}_6\text{H}_4\text{Me}\cdot\text{NH}\cdot\text{N}(\text{OH})\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_3\text{H}$, being first formed, which combines with a second molecule of diazosulphanilic acid forming a compound $\text{C}_6\text{H}_4\text{Me}\cdot\text{NH}\cdot\text{N}(\text{OH})\cdot\text{N}(\text{C}_6\text{H}_4\cdot\text{SO}_3\text{H})\cdot\text{N}(\text{OH})\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_3\text{H}$, corresponding with von Pechmann's bisdiazobenzene anilide; and, finally, this is resolved into diazoamidosulphanilic acid and diazotoluene

which, with the remaining toluidine, yields diazo-amidotoluene. The results obtained with diazotoluene and sulphanilic acid in alkaline solution are explained in a similar manner. J. B. T.

Action of Nitrosobenzene on Amido-compounds. By EUGEN BAMBERGER (*Ber.*, 1896, **29**, 102—104; compare Mills, *Trans.*, 1895, 925).—The author has studied the behaviour of numerous amido-compounds towards nitrosobenzene, bases of both the aromatic and the aliphatic series having been included in the investigation, the results of which will be shortly published.

According to Mills (*loc. cit.*), phenylhydrazine gives rise to azobenzene when treated with nitrosobenzene, Walther having obtained aniline; the author, however, has observed the production of *diazohydroxyamidobenzene*, $\text{PhN:N}\cdot\text{N}(\text{OH})\text{Ph}$, crystallising in pale yellow, silky needles, which melt at 126—127°. This substance is also obtained from diazobenzene and phenylhydroxylamine, which are formed when the compound is treated with acids. Analogous diazohydroxy-amido-compounds have been obtained from β -benzylhydroxylamine and β -methylhydroxylamine, namely, *diazobenzenehydroxyamidobenzyl*, $\text{PhN:N}\cdot\text{N}(\text{OH})\cdot\text{CH}_2\text{Ph}$, which melts at 105°, and *paranitrodiazobenzenehydroxyamidomethane*, $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{N:N}\cdot\text{N}(\text{OH})\text{Me}$, which crystallises in silky, golden-yellow needles, and melts at 228°.

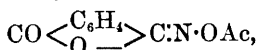
M. O. F.

Influence of Methyl Groups in the Ortho-position in hindering the Formation of Oximes. By FRITZ BAUM (*Ber.*, 1895, **28**, 3207—3212).—Hantzsch (*Abstr.*, 1891, 36) has shown that both ketones and aldehydes, in which substitution has taken place in the two ortho-positions with respect to the carbonyl group, do not yield oximes. Feith and Davies (*Abstr.*, 1892, 314) have also shown that acetylmesitylene yields no oxime, but at higher temperatures reacts with hydroxylamine hydrochloride, according to Beckmann's reaction, yielding acetomesidide. The author has investigated the action of hydroxylamine hydrochloride on dibenzoylmesitylene, mono- and diacetylisodurene, acetylpentamethylbenzene, and mesitylglyoxylic acid, and finds that no oxime is formed in any case; mesitylglyoxylic acid, however, gave cyanomesitylene (m. p. 53°). Ethylic mesitylglyoxylate yields a compound which may be an oxime, and which is being subjected to further investigation.

Acetylmesitylene, mono- and di-benzoylmesitylene, and propionylmesitylene, when treated with phenylhydrazine, yield no hydrazones. When acetylmesitylene is added to concentrated nitric acid, *dimesityldinitroacetyl*, $\text{C}_6\text{H}_2\text{Me}_3\cdot\text{CO}\cdot\text{C}(\text{NO})_2$, is obtained; it crystallises in large, yellowish needles, melts at 141°, and, when boiled with alcoholic soda, yields mesitylcarboxylic acid. J. J. S.

Action of Hydroxylamine on Methylic Phthalate. By GIORGIO ERRERA (*Gazzetta*, 1895, ii, 21—25).—Hydroxylamine acts

on methylic phthalate under various conditions, yielding phthalylhydroxylamine, from which *phthalylacetoxylamine*,



is readily prepared; this crystallises in monoclinic plates melting at 181° , and is sparingly soluble in alcohol or water; $a : b : c = 1.97784 : 1 : 1.11035$; $\beta = 85^\circ 48'$. It is hydrolysed by boiling with water, yielding acetic acid and phthalylhydroxylamine; the latter gives a crystalline *ammonio*-derivative, which is very soluble in water, and readily loses ammonia in the air, giving phthalylhydroxylamine.

W. J. P.

γ -Carbodiphenylimide. By CARL SCHALL (*Ber.*, 1896, **29**, 270—271).—Von Miller and Plöchl have suggested (*Abstr.*, 1895, i, 415) that γ -carbodiphenylimide is a mixture of the liquid α -, and the crystalline, β -compounds; in opposition to this view, the following facts are advanced. (1) With light petroleum, the surface of the γ -compound becomes granular, and is slowly converted into the β -form; the change corresponds exactly with that which takes place when vitreous arsenious anhydride passes into the crystalline modification, and is also slowly produced by gentle heating, during which no α -imide is volatilised. (2) Miller and Plöchl have shown that a concentrated benzene solution of the β -imide, at about the freezing point of benzene, contains, at the most, only traces of the α -compound; such a solution, after concentration under certain conditions, yields only the amorphous γ -compound. (3) When intimately mixed, the α - and β -compounds give a white, opaque mass, which is only viscid if it contains 4 parts of the α -imide. The γ -modification occasionally changes slowly and spontaneously into crystals consisting of needles and plates; it can scarcely be a solid solution, as such should, from analogy, be crystalline and not amorphous.

J. B. T.

Action of Succinic acid on Paramidophenol and its Ethers.

By ARNALDO PIUTTI (*Ber.*, 1896, **29**, 84—86).—*Parahydroxyphenylsuccinimide*, $\begin{matrix} \text{CH}_2\text{CO} \\ | \\ \text{CH}_2\text{CO} \end{matrix} > \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{OH}$, is obtained by fusing succinic

acid with paramidophenol in molecular proportion; it crystallises in lustrous, colourless prisms, and melts at 275 — 276° . Hot potash converts it into *parahydroxyphenylsuccinamic acid*, which dissolves in water, alcohol, and acetic acid, and melts at 171 — 172° ; the *barium* and *alkali* salts are readily soluble in water, the *lead* and *silver* salts are crystalline, and the *copper* salt is insoluble in water.

Paramethoxyphenylsuccinimide is produced on heating paranisidine hydrochloride or methacetin with succinic acid at 190° , and crystallises in colourless, prismatic needles, which melt at 162 — 163° ; hydrolysis gives rise to *paramethoxyphenylsuccinamic acid*, which crystallises from water, and melts at 156 — 157° .

Parethoxyphenylsuccinimide (*pyrantine*) is obtained by fusing succinic acid with phenacetin, or with paraphenetidine hydrochloride; it crystallises in colourless, prismatic needles, and melts at 155° . Succinic acid and phenetidine are formed when the substance is

treated with hot hydrochloric acid, and fusion with potassium hydrogen sulphate brings about the same result; coloration is developed by nitric acid, chromic acid, chlorine water, and ammonia, whilst fusion with potash, and treatment of the aqueous extract with a solution of calcium hypochlorite, yields a red liquid. *Parethoxyphenylsuccinamic acid* is obtained by hydrolysing the foregoing derivative; it crystallises from hot water in nacreous leaflets, and melts at 160—161°. The *sodium* salt is the soluble form of pyranine, and possesses valuable physiological properties which recommend its application as a febrifuge. M. O. F.

Action of Phenyl isocyanate on Amido-acids. By CARL PAAL and FRITZ GANSER (*Ber.*, 1895, 28, 3227—3234; compare *Abstr.*, 1894, i, 332).—In continuation of their work on amido-acids, the authors have studied the action of phenyl isocyanate on the alkali salts of the three amidocinnamic acids, of sulphanilic acid, and sarcosine.

Orthophenylureidocinnamic acid,



crystallises in very small, felted needles, melts at 236°, is insoluble in water, only sparingly soluble in chloroform, carbon bisulphide, and ether, but readily in hot alcohol and acetic acid. The *alkali* salts are not soluble in concentrated, alkaline liquids; the *silver* salt forms an amorphous mass, which is practically insoluble in water, and is extremely sensitive to light. The *ethylic* salt crystallises in needles, melts at 112°, and is readily soluble in most organic solvents. When the acid is reduced with sodium amalgam and water, it yields *ortho-phenylureidophenylpropionic acid*, which melts at 168°, and is readily soluble in hot alcohol, acetone, and ethylic acetate. The *dibromide*, $\text{NHPb} \cdot \text{CO} \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{CHBr} \cdot \text{CHBr} \cdot \text{COOH}$, melts at 227°, and is readily soluble in alcohol and ethylic acetate, but only sparingly in most other organic solvents.

Metaphenylureidocinnamic acid melts at 249°, and is more sparingly soluble in most solvents than the ortho-acid. The *ethylic* salt crystallises in needles, melts at 198°, and is readily soluble in chloroform and ethylic acetate. The *ammonium*, *sodium*, and *silver* salts resemble those of the ortho-acid. The *dibromide* crystallises in small plates, and melts at 240°. *Metaphenylureidophenylpropionic acid* melts at 180°.

Paraphenylureidocinnamic acid crystallises in brilliant glistening needles, and melts at 252°; the *ethylic* salt melts at 204°, and the dibromide begins to decompose at 165°. *Paraphenylureidophenylpropionic acid* melts at 218°, and is practically insoluble in ether.

Paraphenylureidobenzenesulphonic acid, $\text{NHPb} \cdot \text{CO} \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{SO}_3\text{H}$, obtained from sodium sulphanilate and phenyl isocyanate, crystallises in colourless needles or prisms, and begins to decompose at 270°, but is not completely melted at 300°. It is practically insoluble in ether, chloroform, and benzene, but readily in ethylic alcohol, acetone, and acetic acid. The *calcium* salt crystallises from its hot aqueous solution in glistening, rhombic plates, which contain $3\frac{1}{2}\text{H}_2\text{O}$.

The *barium* salt is anhydrous, and is only sparingly soluble in hot water. The *silver* salt crystallises from hot water in large prisms, and is not decolorised by exposure to light. The *ethylic* salt crystallises in colourless needles, melts at 155° , and is readily soluble in ether, alcohol, acetone, &c.

ab-Methylphenylureidoacetic acid, $\text{NHPh}\cdot\text{CO}\cdot\text{NMe}\cdot\text{CH}_2\cdot\text{COOH}$, crystallises in needles, melts at 102° , and is insoluble in ether and chloroform, but readily dissolves in sodium hydroxide, boiling water, ethylic acetate, and water. The silver salt could not be obtained; the *ethylic* salt crystallises in small needles, and melts at 75° .

J. J. S.

Derivatives of Metadibromoparahydroxybenzaldehyde. By CARL PAAL and G. KROMSCHÖDER (*Ber.*, 1895, 28, 3234—3236; compare this vol., i, 40).—The dibromohydroxybenzaldehyde [$\text{Br}_2:\text{OH} = 3:5:4$], previously described, readily combines with aniline to form *dibromoparahydroxybenzylideneaniline*, $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{Br}_2\cdot\text{CH}\cdot\text{NPh}$. It is readily soluble in warm alcohol and in most organic solvents, crystallises in compact, red crystals, or from alcohol in small, metallic, violet coloured plates containing alcohol of crystallisation. It melts at 147° .

Metadibromoparahydroxybenzylideneparatoluidine crystallises from its alcoholic solution in plates, which are characterised by a blue, metallic lustre, and melts at 157° .

Metadibromoparahydroxybenzylidene- α -naphthylamine crystallises in yellowish needles, melts at 146° , and does not combine with alcohol.

Metadibromoparahydroxybenzaldoxime crystallises in short, white needles, melts at 194° , and is readily soluble in alcohol, ether, and ethylic acetate.

Metadibromoparahydroxybenzoic acid, obtained by the oxidation of the aldehyde with potassium permanganate (1 per cent. solution), crystallises in colourless needles and melts at 268° . J. J. S.

Isomerism of Trithioaldehydes. By EMIL WÖRNER (*Ber.*, 1896, 29, 139—160).—Baumann and Fromm (*Abstr.*, 1889, 852; 1890, 25 and 26; 1891, 1008 and 1050) have shown that benzaldehyde, anisaldehyde, methyl- and isobutylsalicyl-aldehyde, cinnamaldehyde, and furfuraldehyde each yield two stereoisomeric trithioaldehydes, a lower melting, or α -, form, and a higher melting, or β -, form. Kopp (*Abstr.*, 1894, i, 128) found that the three hydroxybenzaldehydes yield, each, one trithio-derivative, which he termed the β -modification, as it was not changed by the action of iodine. The author has repeated some of Kopp's experiments, and has arrived at similar results. Thus, with parahydroxybenzaldehyde under the most varying conditions, only a single trithio-compound could be obtained; it crystallises with 2 mols. of benzene (Kopp states 3 mols.), which it partially loses on exposure to the air, and melts at 215° .

Parabenzylloxybenzaldehyde, obtained by shaking the hydroxyaldehyde in strong alkaline solution with the requisite quantity of benzylic chloride, crystallises in short needles, melts at 72° , and is readily soluble in alcohol, chloroform, benzene, and ether. If hydrogen

sulphide is passed into an alcoholic solution to which alcoholic hydrogen chloride has been added, α -trithioparabenzylloxybenzaldehyde is obtained; it crystallises in colourless needles, melts at 127° , and is sparingly soluble in alcohol and ether, but readily in chloroform, benzene, and acetone. When treated with iodine, it passes into the β -modification, which also crystallises in colourless needles, melts at 198 — 199° , contains 2 mols. of benzene of crystallisation, and is more sparingly soluble in all solvents than the α -compound. By using $\frac{1}{4}$ vol. of alcoholic hydrogen chloride to 1 vol. of a 5 per cent. solution of the benzylbenzaldehyde, about equal quantities of the α - and β -modifications are obtained.

Vanillin yields only one trithiovanillin, which melts at 235 — 237° , and is only sparingly soluble in alcohol, benzene, and ether, more readily in chloroform and acetone; when the crystals are boiled with benzene, they take up 2 mols. of benzene of crystallisation. Trithio-benzoylvanillin, obtained by the action of benzoic chloride on trithiovanillin, crystallises in colourless needles, begins to sinter at 155° , and melts at 164° . Benzoylvanillin melts at 75° , and is readily soluble in alcohol, chloroform, and ether.

Methylvanillin yields two isomeric trithio-derivatives, which may be separated by means of benzene. α -Trithiomethylvanillin crystallises in small needles, melts at 168° , and is extremely readily soluble in benzene, but only sparingly so in alcohol; when treated, in benzene solution, with iodine, it is transformed into the β -compound, which crystallises with 2 mols. of benzene or thiophen, and melts at 220° .

α -Trithiopiperonal crystallises in small, colourless needles, melts at 183° , is sparingly soluble in alcohol or ether, and readily in chloroform, acetone, and benzene. β -Trithiopiperonal melts at 236° , and is more sparingly soluble than the α -compound.

Trithiogentisic aldehyde apparently exists in one form only; this crystallises in small, white needles, melts and decomposes at 190° , and is very readily soluble in alcohol.

α -Trithiodimethylgentisic aldehyde is a colourless, crystalline powder, melts at 95 — 96° , and is readily soluble in benzene, acetone, and chloroform. The β -compound crystallises with 2 mols. of benzene and melts at 180° . It is practically insoluble in alcohol, and only sparingly soluble in chloroform.

α -Trithiocumaldehyde crystallises in long, white needles, and melts at 165° ; the β -compound could not be obtained directly, but only by the action of iodine on the α -isomeride; it crystallises with 3 mols. of benzene, and melts at 205° .

α -Trithiometatolualdehyde crystallises in white needles and melts at 144° ; the β -isomeride crystallises in white, glistening needles, which contain 3 mols. of benzene, and melts at 225° .

α -Trithioparatolualdehyde melts at 149 — 150° , and the β -compound at 180° ; the latter crystallises with 3 mols. of benzene.

α -Trithio-orthobromobenzaldehyde melts at 75° , is only sparingly soluble in alcohol, but readily in ether, benzene, chloroform, and acetone; the β -isomeride melts at 155° , and crystallises with 1 mol. of benzene.

α -Trithioparabromobenzaldehyde is readily soluble in benzene, and

crystallises in small needles, which melt at 174° . The β -compound crystallises with 1 mol. of benzene, melts at 203° , and is more sparingly soluble than the α -isomeride.

Metanitrobenzaldehyde yields a trithio-derivative, which melts at 180 — 190° ; it was found impossible to purify the compound, as it is insoluble in all organic solvents. Orthonitrobenzaldehyde gave a similar result.

Metanitrocumaldehyde gave only one trithio-derivative, which melts at 118° , and is not acted on by iodine. Metanitroanisaldehyde melts at 72° , whereas Einhorn and Grabfield (Abstr., 1888, 478) give 83.5° as the melting point. A dinitroanisaldehyde, melting at 86° , was also obtained. Trithiometanitroanisaldehyde is a yellowish, crystalline powder, and melts at 108° ; the trithiodinitroaldehyde melts at 188° , is readily soluble in benzene, chloroform, and acetone, but only sparingly in alcohol or ether.

The author summarises his results as follows.

1. Substituted aromatic aldehydes yield two stereoisomeric trithio-derivatives only when the substituting groups are of a positive or indifferent nature. Aldehydes with negative substituting groups yield one trithio-aldehyde, namely, the β -modification. If the negative character of the hydroxyl group of a phenolic aldehyde is changed by methylation, &c., then the resulting compound yields two isomeric trithio-derivatives.

2. All α -trithioaldehydes may be converted into the β -modifications by means of iodine.

3. The trithioaldehydes are most easily obtained from phenolic aldehydes or aldehydes containing negative groups; if positive groups are present, polymerides of high molecular weight are apt to be formed.

J. J. S.

Metadihydroxyphenyl Ketones. By ADOLPH CLAUS and M. HUTH (*J. pr. Chem.*, 1896, [2], 53, 39—42).—By acetylating the alkylic ethers of resorcinol (by treating them with acetic chloride and aluminium chloride in carbon bisulphide), it is possible to obtain, according to the conditions of the experiment, the dialkyloxyacetophenone, the alkyloxyhydroxyacetophenone, or dihydroxyacetophenone itself. The compound last mentioned melts at 178° , and is therefore not identical with that (m. p. 142°) obtained by Nencki and Sieber (Abstr., 1881, 591) from resorcinol by acting on it with glacial acetic acid and zinc chloride. This lack of identity extends to the derivatives of the two compounds, as will be seen from the following list of melting points.

	Nencki and Sieber.	Claus and Huth.
Dihydroxyaceto-phenone.....	142°	178°
Oxime therefrom	202° (decomposes)	223 — 225° (decomposes).
Monethyl ether..	48°	108°
Diethyl ether...	68 — 69°	152°
Oxime therefrom	122°	240° (decomposes).

The authors note a curious interchange between these two com-

pounds and their derivatives, which seems to betoken an alteration of orientation, brought about by the influence of the alkyl groups. The identity of composition and molecular weight of the two dihydroxyacetophenones has been established. A. G. B.

Introduction of two Acetyl Groups into Aromatic Hydrocarbons. By FRITZ BAUM and VICTOR MEYER (*Ber.*, 1895, 28, 3212—3215).—Hitherto it has been found impossible to introduce two acetyl groups into aromatic hydrocarbons by the Friedel-Crafts method, but the authors show that a diacetyl derivative of durene may be obtained if the action is carried on without prolonged heating, and in the presence of an excess of acetic chloride; if, however, the mixture is heated for some time, as in the usual Friedel-Crafts synthesis, the monacetyl derivative alone is obtained. Benzene and mesitylene apparently do not yield diacetyl derivatives under similar conditions.

Diacetyldurene melts at 178°, distils between 323 and 326°, and crystallises from ether in glistening, six-sided plates.

Diacetylisodurene melts at 121° and distils at 312—317°.

Acetylisodurene is an oil, and boils at 255—260°.

Dipropionyldurene melts at 176° and boils at 330—335°.

Propionyldurene melts at 79° and distils at 265—270°.

The authors have not yet proved that the second acetyl group does not replace one of the methyl groups of durene. J. J. S.

Formation and Hydrolysis of Ethereal Salts. By VICTOR MEYER (*Ber.*, 1895, 28, 3197—3201; compare *Abstr.*, 1894, i, 243, 463; 1895, i, 93, 228, 466).—The author now shows that phenylacetic acid is much more readily etherified than benzoic acid. Thus, a solution of phenylacetic acid in methylic alcohol, containing only 3 per cent. of hydrochloric acid, yields 50 per cent. of ethereal salt after five minutes; benzoic acid under the same conditions yields no trace of ethereal salt. This points to the fact that the two methylene hydrogen atoms in phenylacetic acid exert no restraining influence on the formation of ethereal salts, whereas the two methin hydrogen atoms in benzoic acid do.

The relationship between the formation of ethereal salts and the hydrolysis of the corresponding nitriles is not so simple as it is generally considered. For instance, triphenylacetic acid is etherified with difficulty and triphenylacrylic acid readily, but the nitrile of the former acid is much more easy to hydrolyse than that of the latter.

It has been previously shown that mesitylformic (mesitylenecarboxylic) acid, when treated for 12 hours in the cold, yields no ethereal salt, whereas, at the boiling point of the alcohol, a considerable amount of ethereal salt is formed. It is now shown that, if hydrogen chloride is kept passing through a solution of this acid in methylic alcohol (at 0°) during a week, no less than 26 per cent. is converted into the ethereal salt, and, at the end of two weeks, 46 per cent. Symmetrical trinitrobenzoic acid, when treated in the same way for a week, gave only 0.7 per cent. of ethereal salt. The mono-substituted derivatives of benzoic acid, in which the substituting groups were CH₃, Cl, Br, I, and NO₂, have been investigated, and, in each case, the ortho-acid

was the one which took longest to etherify, and the corresponding ethereal salt the one most difficult to hydrolyse.

Other alcohols besides methylic alcohol have been tried, and yield similar results. J. J. S.

A New Phenomenon in the Formation of Ethereal Salts by the action of Alcohol and Hydrogen Chloride on Aromatic Acids. By A. SHUKOFF (*Ber.*, 1895, **28**, 3201—3202).—The author has studied the action of methylic alcohol and hydrogen chloride on benzoic and phenylacetic acids; he finds that a given concentration of the hydrogen chloride gives the maximum of ethereal salt in a given time, and that a stronger or weaker alcoholic solution of the hydrogen chloride yields smaller quantities of ethereal salt. Thus at 0° phenylacetic acid gives a maximum of methylic salt when treated with a solution containing 40 grams of hydrogen chloride to 100 of methylic alcohol; at 22°, benzoic acid gives a maximum of ethereal salt with 50 parts of hydrogen chloride to 100 of alcohol.

Heinrich Goldschmidt suggests that the more concentrated solutions of hydrogen chloride in alcohol readily form the alkyl chloride and water, and that it is the water thus formed which has a retarding influence on the formation of ethereal salts. J. J. S.

Etherification by means of Alcoholic Hydrogen Chloride. By HEINRICH GOLDSCHMIDT (*Ber.*, 1895, **28**, 3218—3227).—The author has made experiments on the velocity of etherification of benzoic acid, by means of alcohol, in the presence of varying quantities of hydrogen chloride; the results show that the velocity of etherification in the case of dilute solutions of hydrogen chloride is proportional to the concentration of the hydrogen chloride, but the addition of even small quantities of water retards the velocity to a considerable extent. Hydrogen bromide has very much the same influence on the velocity of etherification as hydrogen chloride, but picric acid has far less influence. Substituted benzoic acids are etherified at different rates by alcoholic hydrogen chloride; in all cases, the ortho-substituted acids are much more slowly etherified (V. Meyer, this vol., i, 228). As a rule, substitution in the meta-position increases the velocity, except in the case of the nitro-group, and para- are more slowly etherified than meta-compounds. The author also confirms V. Meyer's statement that phenylacetic acid is more easily etherified than benzoic acid. J. J. S.

Formation of Ethereal Salts from Acids and Alcohols. By RUDOLF WEGSCHEIDER (*Ber.*, 1895, **28**, 3127—3128; compare *Abstr.*, 1895, i, 499).—The action of methylic alcohol on hemipinic acid, in presence of an eighth part of its volume of concentrated sulphuric acid gives rise to the β -monomethylic salt; etherification by means of sulphuric acid has, therefore, the same result as when hydrogen chloride is employed, and the author in consequence holds the view that in the former case also etherification depends on the intermediate production of an additive compound. When equal volumes of methylic alcohol and sulphuric acid are used, the normal salt of hemipinic acid is

formed; symmetrical tribromobenzoic acid is also partially etherified when thus treated, although, under the conditions first described, the last-named acid yields no ethereal salt. There is no appreciable formation of ethereal salt when a mixture of methylic alcohol and sulphuric acid acts on hydrogen potassium hemipinate during a short period.

When hemipinic acid is heated with methylic alcohol at 100° , α -monomethylic hemipinate is produced, probably owing to the intermediate formation of the anhydride, as this substance is obtained in small quantity when hemipinic acid is heated at 100° , benzoic acid, moreover, yields no ethereal salt under these conditions. The formation of the α -modification in the absence of sulphuric acid or hydrogen chloride clearly indicates that the effect produced by these agents is not due to dehydrating action. M. O. F.

Pseudophenylacetic acid. By EDUARD BUCHNER (*Ber.*, 1896, **29**, 106—109).—The author proposes to apply the names pseudophenylacetic acid, pseudotolylacetic acid, &c., to the acids which are obtained by the action of ethylic diazoacetate on the aromatic hydrocarbons, and are isomeric with phenylacetic acid, &c. *Sodium pseudophenylacetate* is obtained as a crystalline powder by the action of sodium ethoxide on the ethylic salt. It cannot be recrystallised, gradually increases in weight when preserved in dry air, and is at once oxidised by potassium permanganate. Like the ethylic salt and the amide, it forms a cherry-red solution in concentrated sulphuric acid, the colour gradually changing to indigo-blue. *Pseudophenylacetamide* crystallises from water in large, vitreous tablets, which melt at 141° . When hydrolysed by aqueous soda, it yields an unsaturated acid, which melts at about 71° , and does not give the characteristic reaction of the amide with sulphuric acid. *Sodium pseudotolylacetate* closely resembles the corresponding salt of pseudophenylacetic acid. Pseudotolylacetic acid unites with four atoms of bromine to form an unstable *tetrabromide*, which loses hydrogen bromide when kept, a solid substance being left, which has the formula $C_6H_4Br_3O_2$. This compound cannot be recrystallised, but may be reprecipitated from its solution in alkalis; it melts at 80 — 85° . The corresponding *derivative* of pseudophenylacetic acid melts at 84 — 86° . When pseudotolylacetic acid is passed through a red-hot tube, about 10 per cent. of paraxylene is formed. Pseudophenylacetic acid yields about 7 per cent. of terephthalic acid when oxidised with nitric acid, whilst this acid is accompanied by benzoic acid when alkaline potassium permanganate is used. The constitution of pseudophenylacetic acid is best represented by the formula $COOH \cdot CH < \begin{smallmatrix} CH \cdot CH \cdot CH \\ | \\ CH \cdot CH \cdot CH \end{smallmatrix}$, which admits of a simpler explanation of the reactions of the acid than that proposed by V. Meyer (*Ber.*, 1890, **23**, 617), in which the $COOH \cdot CH$ group is attached at the para- instead of the ortho-positions.

A. H.

Tetramethylbenzoic acids. By ADOLPH CLAUS (*J. pr. Chem.*, 1895, [2], **52**, 529—532).—In reference to V. Meyer's recent publication (this vol., i, 170), the author draws attention to the work which

has been done by himself and his pupils on the oxidation of the methyl duryl ketones (Abstr., 1888, 275; 1889, 50). Attempts to purify the tetramethylbenzoic acids then described have succeeded to some extent, and it is shown that the 2 : 3 : 5 : 6-acid melts at 127°, not 109° (*loc. cit.*).

The oxidation of symmetrical tetramethylbenzoic acid by permanganate yields, under all conditions, dimethylbenzenetricarboxylic acid, whilst similar treatment of asymmetrical tetramethylbenzoic acid yields a dicarboxylic acid, in which the new carboxyl group is in the para-position, for by distillation with soda-lime it gives pseudocumene. Details of this research will follow shortly.

Contrary to Victor Meyer's rule, all three acids are equally easily etherified by hydrogen chloride in methylic and ethylic alcohol. The methylic and ethylic salts of symmetrical tetramethylbenzoic acid are crystalline, the former melting at 79–81°, and the latter at 47–48°. The methylic and ethylic salts of the other acids are viscid oils.

Some criticisms of V. Meyer's paper are given.

A. G. B.

Action of Ammonia on Ethylic Benzoylacetate. By CARL GOLDSCHMIDT (*Ber.*, 1896, 29, 105).—Ammonia unites with ethylic benzoylacetate to form an *additive product*, $\text{COPh}\cdot\text{CH}_2\cdot\text{COOEt}\cdot\text{NH}_3$, which crystallises from alcohol in plates, having a satiny lustre, and melting at 178°. It sublimes when heated, and yields ammonia when treated with aqueous soda. Methylamine converts ethylic benzoylacetate into a white compound which gradually loses water and changes into *ethylic β -methylimidophenylpropionate*, $\text{NMe}\cdot\text{CPh}\cdot\text{CH}_2\cdot\text{COOEt}$. A. H.

Regularity in the Decomposition of Aromatic Ketonic Acids. By FELIX MUHR (*Ber.*, 1895, 28, 3215–3218).—Victor Meyer has previously shown (Abstr., 1895, i, 467) that symmetrical trimethyl- β -benzoylpropionic acid is decomposed by hydriodic acid into mesitylene and succinic acid. The author shows that the same decomposition may be brought about by heating the acid for five hours at 150° with hydrochloric acid.

Paramethylbenzoylpropionic acid, obtained by the action of a solution of toluene in carbon bisulphide on succinic anhydride in the presence of aluminium chloride, melts at 117°, and is not decomposed when heated with hydrochloric acid at 150°. Benzoylpropionic acid also is not acted on.

Metadimethylbenzoylpropionic acid (obtained from metaxylene), crystallises in colourless needles, melts at 106°, and is completely decomposed into metaxylene and succinic acid when heated with hydrochloric acid.

Orthodimethylbenzoylpropionic acid melts at 105°, and is not decomposed under the usual treatment.

Paradimethylbenzoylpropionic acid melts at 62°, whereas Claus gives 84° as the melting point, and is partially decomposed when heated at 150° with hydrochloric acid.

Asymmetrical trimethylbenzoylpropionic acid (from pseudocumene) melts at 98°, and is also partially decomposed when heated with hydrochloric acid.

Symmetrical tetramethylbenzoylpropionic acid (from durene) melts at 117° , and is decomposed in a similar manner, *pentamethylbenzoylpropionic acid* (white plates melting at 104°), is also decomposed, whereas *ethylbenzoylpropionic acid*, which crystallises in slender, lustrous needles, and melts at 90° , yields only traces of its decomposition products.

Orthomethylethylbenzoylpropionic acid, which forms very long, slender, lustrous needles melting at 78° , and *isopropylbenzoylpropionic acid*, crystallising in needles melting at 72° , are both practically unacted on when heated with hydrochloric acid at 150° , and about 50 per cent. of *paramethylisopropylbenzoylpropionic acid* (colourless plates melting at 70°) is decomposed, after heating for nine hours at 200° with hydrochloric acid.

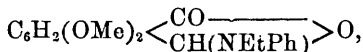
From these results it follows that only those acids are decomposed in which the side chain containing the carboxylic group is in the ortho-position relatively to one or both of the alkyl groups. J. J. S.

Preparation of Ethylic Benzyldieneacetoacetate. By EMIL KNOEVENAGEL (*Ber.*, 1896, **29**, 172—174).—Ethylic acetoacetate and benzaldehyde in molecular proportion are mixed, cooled at -5° , piperidine (1 gram), diluted with two parts of alcohol, is added, and the liquid allowed to remain at the same temperature during 12—24 hours; the crystals are then separated and purified. The yield is 95 per cent. of the theoretical, and 100 grams of ethylic acetoacetate can be conveniently employed at once. The action probably takes place in two stages, benzyldenedipiperidine, $\text{CHPh}(\text{C}_5\text{NH}_{10})_2$, is first formed, and reacts with the ethylic acetoacetate, piperidine being regenerated. Diethylamine acts like piperidine. At the ordinary temperature, ethylic benzyldenediacetoacetate alone is formed from ethylic acetoacetate and benzaldehyde. J. B. T.

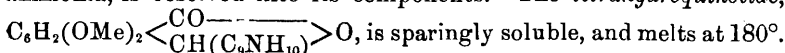
Tautomerism of the Orthaldehydic Acids. By CARL LIEBERMANN (*Ber.*, 1896, **29**, 174—183).—*Opianic acid semicarbazone*, $\text{COOH}\cdot\text{C}_6\text{H}_2(\text{OMe})_2\cdot\text{CH}\cdot\text{N}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2$, is readily prepared by the action of opianic acid, in glacial acetic acid solution, on semicarbazide in aqueous solution; on the addition of water to the glacial acetic acid solution, it crystallises out in lustrous needles, melting at 187° . It quickly dissolves at the ordinary temperature in soda, and in concentrated, but not in dilute, hydrochloric acid; if the acid solution is immediately diluted, the compound is reprecipitated. When heated with glacial acetic acid, the semicarbazone yields opiazone, $\text{C}_6\text{H}_2(\text{OMe})_2\cdot\text{CH}\cdot\text{N}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}$; whilst boiling with concentrated hydrochloric acid converts the semicarbazone into normethylopiazone, $\text{HO}\cdot\text{C}_6\text{H}_2(\text{OMe})_2\cdot\text{CH}\cdot\text{N}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}$. *Methylic n-opianate semicarbazone*, $\text{COOMe}\cdot\text{C}_6\text{H}_2(\text{OMe})_2\cdot\text{CH}\cdot\text{N}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2$, prepared from methylic *n*-opianate and semicarbazide, crystallises in needles, melts at 204° , and is insoluble in cold soda. Ethylic ψ -opianate slowly reacts with semicarbazide, and yields opianic acid semicarbazone (see above); evidently the salt is slowly hydrolysed by the water, and the free acid then condenses with the carbazide.

Phthalaldehydic acid semicarbazone, $\text{COOH}\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{N}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2$, prepared, like the opianic derivative, from phthalaldehydic acid, crystallises in needles, melts at 202° , dissolves in cold soda, and when boiled with glacial acetic acid, is converted into phthalazone.

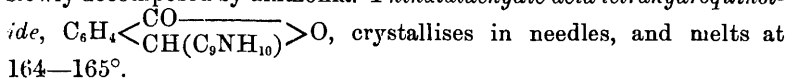
Opianic acid and phthalaldehydic acid combine in alcoholic solution, with various primary and secondary bases. The resulting compounds crystallise readily, are insoluble in soda at the ordinary temperature, and are resolved into their components when boiled with baryta water, and by the action of alcoholic, and generally of aqueous, hydrogen chloride, the latter giving first yellow compounds. *Opianic acid α -naphthylamide*, $\text{C}_6\text{H}_2(\text{OMe})_2\langle\text{CO}\overline{\text{CH}(\text{NH}\cdot\text{C}_{10}\text{H}_7)}\rangle\text{O}$, melts and decomposes at 212° . The *β -naphthylamide* melts at 213° , dissolves, and gives an orange-red coloration with concentrated sulphuric acid, and, by the prolonged action of soda (10–15 per cent.), is converted into the *sodium salt*, $\text{COONa}\cdot\text{C}_6\text{H}_2(\text{OMe})_2\cdot\text{CH}\cdot\text{N}\cdot\text{C}_{10}\text{H}_7$, which crystallises in long plates; the free *opian- β -naphthylamic acid*, prepared by the cautious addition of acetic acid to the sodium salt, is unstable, and melts and decomposes at 195 – 200° . Hydrochloric acid gives a yellow coloration, which rapidly disappears, probably indicating the formation of a hydrochloride, subsequent additions of acid momentarily restore the colour, and, finally, the greater portion of the substance dissolves. The *methyl salt*, $\text{COOMe}\cdot\text{C}_6\text{H}_2(\text{OMe})_2\cdot\text{CH}\cdot\text{N}\cdot\text{C}_{10}\text{H}_7$, is prepared from methyl *n*-opianate and *β -naphthylamine*; it crystallises in plates, and melts at 131° . The *ethylamide*,



crystallises in plates, melts at 116 – 117° , and, by the action of ammonia, is resolved into its components. The *tetrahydroquinolide*,



is sparingly soluble, and melts at 180° . The *tetrahydroquinoldide*, $\text{C}_6\text{H}_2(\text{OMe})_2\langle\text{CO}\overline{\text{CH}(\text{C}_{10}\text{NH}_{12})}\rangle\text{O}$, melts at 180° , gives a yellow coloration with sulphuric acid, and is only slowly decomposed by ammonia. *Phthalaldehydic acid tetrahydroquinolide*,



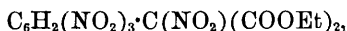
crystallises in needles, and melts at 164 – 165° . The preceding results show that towards semicarbazide, opianic acid and phthalaldehydic acid react as true aldehydic acids, $\text{COOH}\cdot\text{R}\cdot\text{CHO}$; towards primary or secondary amines they react as hydroxyphthalides, $\text{R}''\langle\text{CO}\overline{\text{CH}(\text{OH})}\rangle\text{O}$, if the amides are of medium basicity, but they do not react with feeble bases such as diphenylamine, nor with strong ones like piperidine, as in this case the tendency towards salt formation is too great. Tertiary amines are without action on the aldehydic acids. It is possible that when opianic acid is dissolved in alcohol, some *ψ -ethylic salt* is formed, but this explanation of the results is scarcely satisfactory, as the *ψ -ethylic salt* is without action on *β -naphthylamine* under the conditions

described above, and the naphthylamide is formed if acetone or hot water is employed as solvent in place of alcohol. Probably the salt, $\text{CHO}\cdot\text{R}\cdot\text{COO}\cdot\text{NH}_3\text{R}$, is first formed, which, by condensation, is converted into the closed chain, $\text{R}''\text{C} \begin{smallmatrix} \text{CO}\cdot\text{O} \\ \diagup \quad \diagdown \\ \text{CH}\cdot\text{NHR} \end{smallmatrix}$, and then from this by the action of alkali, the salt $\text{COONa}\cdot\text{R}\cdot\text{CH}\cdot\text{NR}$, is produced. This is in accordance with the behaviour of the β -naphthylamide, and explains the difference between the primary and secondary amines; it is possible that the formulæ given above for the amides may require amendment in this sense.

J. B. T.

Ethyllic 2 : 4 : 6-Trinitrophenylmalonate. By C. LOBING JACKSON and J. I. PHINNEY (*Ber.*, 1895, **28**, 3066—3067).—In addition to the form that melts at 58° (not 59° , as previously stated), there is a form which crystallises differently and melts at 64° ; this can be obtained from a solution of the first form by sowing in it some of the crystals that melt at 64° . The authors have not yet been able to convert this second form into the first, nor have they succeeded in again preparing the first by the action of picryl chloride on ethyllic sodiomalonate.

Ethyllic trinitrophenylmalonate, $\text{C}_6\text{H}_2(\text{NO}_2)_3\cdot\text{CH}(\text{COOEt})_2$, is converted by nitric acid into the white nitrite,



melting at 109° ; prolonged heating with nitric acid oxidises it to the *tartronate*, $\text{C}_6\text{H}_2(\text{NO}_2)_3\cdot\text{C}(\text{OH})(\text{COOEt})_2$, which melts at 117° ; and hydrolysis with dilute sulphuric acid converts it into 2 : 4 : 6-trinitrophenylacetic acid, $\text{CH}_2(\text{NO}_2)_3\cdot\text{CH}_2\cdot\text{COOH}$, which melts at 161° , and, when crystallised from alcohol or water, loses carbonic anhydride and yields symmetrical trinitrotoluene.

C. F. B.

Condensation of Simple Ketones with Ethyllic Succinate and with Ethyllic Pyrotartrate in the presence of Sodium Ethoxide. By HANS STORBE (*Ber.*, 1895, **28**, 3191—3195; compare *Abstr.*, 1895, i, 142 and 410).—In continuation of his work, the author has investigated the products formed by the condensation of benzophenone with ethyllic succinate under the influence of sodium ethoxide. The chief product is *ethyllic hydrogen diphenylitaconate*, $\text{CPh}_2\cdot\text{C}(\text{COOEt})\cdot\text{CH}_2\cdot\text{COOH}$ or $\text{CPh}_2\cdot\text{C}(\text{COOH})\cdot\text{CH}_2\cdot\text{COOEt}$; it melts at $124\cdot5$ — $125\cdot5^\circ$, is not hydrolysed by boiling with hydrochloric acid, but with alkalis gives γ -diphenylitaconic acid, which melts and decomposes at 168 — 169° . A solution of bromine in chloroform has no action on the acid, but bromine in the presence of water converts it into β -bromo- γ -diphenylparaconic acid, $\text{COOH}\cdot\text{CBr}\cdot\text{CPh}_2 \begin{smallmatrix} \diagup \quad \diagdown \\ \text{CH}_2\cdot\text{CO} \end{smallmatrix} \text{--} \text{O}$, which melts at $166\cdot5^\circ$ with liberation of gas. When reduced, the bromo-acid yields diphenylparaconic acid, and, when boiled with water, the corresponding aconic acid.

No acid isomeric with diphenylitaconic acid could be isolated from the products of the action of benzophenone on ethyllic succinate.

Benzophenone, when treated with ethyllic pyrotartrate in a similar

manner, gave *ethylic hydrogen α-methyl-γ-diphenylitaconate*, which melts at 143·5—144·5°. When hydrolysed, the ethylic salt yields the corresponding acid, $\text{C}_6\text{H}_5\cdot\text{C}(\text{COOH})\cdot\text{CHMe}\cdot\text{COOH}$, which melts and decomposes at 179—180°. No isomeric acid was obtained.

Dibenzyl ketone and ethylic succinate, in the presence of sodium ethoxide, gave the monethylic salt of the dibasic acid,



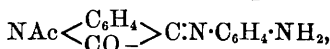
The acid melts at 146—147°, and the ethylic hydrogen salt at 127·5—129°.

The author is at present engaged in trying to find out the constitution of the ethylic hydrogen diphenylitaconate mentioned above.

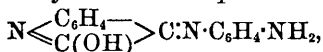
J. J. S.

Sulphamic acids of the Aromatic Series. By CARL PAAL and H. JÄNICKE (*Ber.*, 1895, **28**, 3160—3167; compare *Abstr.*, 1894, i, 365).—Ammonium phenylsulphamate, $\text{NHPh}\cdot\text{SO}_3\cdot\text{NH}_4$, crystallises in white, satiny plates melting at 152°. *Orthotoluidine amidosulphonate* forms colourless prisms which melt at 131°. *Ammonium orthotolylsulphamate* crystallises in concentrically grouped, white needles which melt at 241°. *Paratoluidine amidosulphonate* forms lustrous plates melting at 139°. *Ammonium paratolylsulphamate* crystallises in lustrous, white plates melting at 215°. *Paratolylsulphamic acid*, $\text{C}_6\text{H}_4\text{Me}\cdot\text{NH}\cdot\text{SO}_3\text{H}$, crystallises in concentrically grouped, white needles which melt indefinitely at 175—190°. When the aqueous solution is heated for some time, toluidine sulphate is formed. Sodium nitrite reacts with the aqueous solution to form a white, crystalline salt, which is probably the corresponding sodium nitrosamine-sulphonate. *α-Naphthylamine amidosulphonate* crystallises in lustrous plates. *Ammonium α-naphthylsulphamate* melts at 245°. *α-Naphthylsulphamic acid* crystallises in colourless, flat needles which melt and decompose at 272°. *as-Methylphenylhydrazine amidosulphonate* crystallises in lustrous, white plates melting at 106°, whilst the corresponding *ammonium methylphenylhydrazinesulphonate*, $\text{NMePh}\cdot\text{NH}\cdot\text{SO}_3\cdot\text{NH}_4$, melts at 217°. *as-Diphenylhydrazine amidosulphonate* melts at 120—121°. It has not been found possible to convert this salt into the corresponding ammonium sulphamate. *Amylamine amidosulphonate* crystallises in large, transparent tablets and melts at 185°. *Amylamine amylsulphamate*, $\text{C}_5\text{H}_{11}\cdot\text{NH}\cdot\text{SO}_3\text{H}\cdot\text{NH}_2\cdot\text{C}_5\text{H}_{11}$, is obtained by heating the amidosulphonate with an excess of amylamine at 190—200°, and forms lustrous plates melting at 110°. A. H.

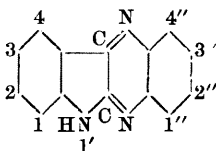
Isatin. EDWARD SCHUNCK and LEO MARCHLEWSKI (*Ber.*, 1896, **29**, 194—203).—When acetyl isatin is warmed with 1 : 2-phenylene-diamine in alcoholic solution, *amidoacetylphenimeisatin*,



is formed; this melts at 285—286° (not 260—261°), and is soluble both in acids and in alkalis. Prolonged boiling with alkaline hydroxides converts it into yellow *2-amidophenimeisatin*,

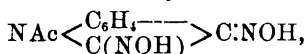


which melts at 260—261°, and dissolves both in alkalis and in acids, yielding even a crystallised hydrochloride. This substance yields azo-dyes; boiling with acetic anhydride converts it into the acetyl derivative described above; and the action of acids—the mere crystallising from hot acetic acid suffices—gives rise to the formation of the substance $\begin{matrix} \text{C}_6\text{H}_4\cdot\text{C}\cdot\text{N} \\ | \\ \text{NH}-\text{C}\cdot\text{N} \end{matrix} > \text{C}_6\text{H}_4$, previously obtained from isatin and 1:2-phenylenediamine, and called isatohydrophenazine (this vol., i, 96), but which it is now proposed to name *indophenazine*; the scheme of numbering proposed for the derivatives of indophenazine will be found adjoined.



3-Methylindophenazine is obtained from methylisatin and ortho-phenylenediamine; it is yellow, and melts at 248°; its white 1'-acetyl derivative melts at 204°. 1:3-Dibromindophenazine, from dibromisatin, is orange coloured, and melts at 275°; its 1'-acetyl derivative is yellow. Nitroindophenazine, from nitroisatin, is yellowish-brown, and has not melted at 305°; its acetyl derivative is yellow.

Acetylisatin, unlike isatin itself, yields a *dioxime*,



which melts and decomposes at 240°.

C. F. B.

Displacement of Isodiazogroups by Cyclic Radicles. II.

By OTTO KÜHLING (*Ber.*, 1896, 29, 165—169; compare Abstr., 1895, i, 182 and 290).—The author finds that in the paranitrophenylpyridine, described in his previous paper (*loc. cit.*), the nitrophenyl group is in the α - and not in the γ -position as stated.

Sodium nitrophenylnitrosamine and nitrobenzene react in the presence of acetic acid to form 4:4'-dinitrodiphenyl (m. p. 233°; compare Fittig, *Annalen*, 124, 276) and 2:4'-dinitrodiphenyl. The nitrophenyltoluene, of melting point 103—104° (compare Bamberger and also Kühling, Abstr., 1895, i, 182, 289), is probably the dipara-compound, and the oily isomeride probably the orthopara-compound.

Paranitrophenylbenzoic acid, [$? 4' : 4$], is obtained on oxidising the solid nitrophenyltoluene with excess of potassium permanganate; it crystallises in colourless needles, melts at 222—225°, and is only sparingly soluble in water, but readily in hot alcohol. When reduced with tin and hydrochloric acid, it yields *paramidophenylbenzoic acid hydrochloride*. The free acid, $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{C}_6\text{H}_4\cdot\text{COOH}$ [$? 4' : 4$], crystallises in small needles or thin plates, melts and decomposes at 106—110°, and is only sparingly soluble in hot water.

Paramido- α -phenylpyridine hydrochloride, $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{C}_5\text{NH}_4\cdot 2\text{HCl}$, obtained by the reduction of the corresponding nitro-compound, forms a colourless, microcrystalline powder, and the *picrate* crystallises in

yellow prisms which melt at 210° . The *base* itself crystallises in small, white plates which rapidly turn red, and melts at 101 – 102° . When the hydrochloride, in alcoholic solution, is treated with sodium nitrite, it yields 2-phenylpyridine (compare Skraup and Cobenzl, Abstr., 1883, 1015). Sodium nitrophenylnitrosamine and quinoline condense in the presence of acetic acid to form *paranitrophenylquinoline*, which separates from its alcoholic solution in the form of yellow, crystalline aggregates, and melts at 158 – 160° . It is soluble in strong acids, yielding yellow solutions.

Paranitrophenylphthalene, obtained by a similar method, crystallises in bright orange needles, melts at 129° , and is practically insoluble in water, but readily soluble in ether. J. J. S.

Formation of Phenylparatolylmethane by the Action of Sodium on Parabromotoluene. By MAX WEILER (*Ber.*, 1896, 29, 111–114).—When parabromo- or parido-toluene is treated with sodium, a certain amount of toluene is produced along with hydrocarbons of high boiling point, two substances being formed, one of which is identical with paratolyl. The second has not yet been obtained pure; it is contained in the fraction boiling at 286 – 293° , and yields paratoluic acid when oxidised with excess of chromic anhydride. If, however, it is oxidised with the calculated amount of chromic anhydride, it is converted into a ketone, which yields an oxime melting at 145 – 150° , and is probably paratolyl phenyl ketone. The second hydrocarbon must, therefore, be phenylparatolylmethane.

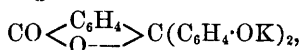
A. H.

Phthaleïns. By JOSEF HERZIG and HANS MEYER (*Ber.*, 1895, 28, 3258–3261).—By the action of methylic iodide on phenolphthaleïn in alkaline solution, 85–90 per cent. of the lactone dimethylic ether is formed; this is scarcely compatible with Friedländer's formula for the sodium salt. Several theories of its formation are discussed; at present, the authors, following von Baeyer, suggest that the decolorisation of phenolphthaleïn solution by means of alkali in excess, is due to the formation of a salt of the acid $C_{20}H_{16}O_5$; the regeneration of the colour, when the liquid is heated, being caused by the dissociation of this salt. Friedländer has described the acetyl derivative of phenolphthaleïn oxime as insoluble in alkali; but this is inconsistent with his formula for it; the substance prepared by him appears to be a mixture of two or three compounds, and is being further investigated. Quinoidal fluoresceïn ethyl ether yields a *monacetyl* derivative which crystallises in highly coloured, yellowish-brown needles melting at 188 – 190° . Nietzki and Schroeter prepared yellow fluoresceïn ethylic ether by the hydrolysis of the quinoidal diethylic derivative, and found that it gives a colourless, acetyl compound; this work has been repeated, and it is found that both the diethylic and ethylic acetyl derivatives, when treated with alcoholic potash and acidified, give a yellow precipitate, the supernatant liquid being fluorescent. On extraction with ether, the solid dissolves, and, after the ether is removed, a white, somewhat unstable compound is obtained; this gradually becomes yellow by repeated recrystallisation, but the

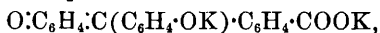
change is more rapid when the substance is heated, and, at 250°, it melts, forming an orange-coloured liquid. The subject is being further investigated.
J. B. T.

Phthaleïns. By JOSEF HERZIG and HANS MEYER (*Ber.*, 1896, **29**, 138—139).—In their preceding paper, the authors failed to mention that Haller and Guyot (*Abstr.*, 1895, i, 376) had already obtained the lactone diethyl ether of phenolphthaleïn. The authors do not agree with those authors' views as to the quinoïdal constitution of the alkali salts of the phthaleïns.
J. J. S.

Constitution of the Alkali Salts of Phenolphthaleïn. By AUGUSTIN BISTRZYCKI and K. NENCKI (*Ber.*, 1896, **29**, 13).—When phenolphthaleïn is dissolved in aqueous potash a *ated* with benzoic chloride, according to Schotten's method, *yl-*phenolphthaleïn, $\text{CO} < \text{O} \begin{smallmatrix} \text{C}_6\text{H}_4 \\ \text{---} \end{smallmatrix} > \text{C}(\text{C}_6\text{H}_4\cdot\text{OBz})_2$, is formed. It crystallises from benzene with 1 mol. of the solvent, in small, colourless prisms, melts when pure at 169°, and is insoluble in dilute alkalis. The potassium salt derived from phenolphthaleïn, therefore, reacts in aqueous solution as though it had the formula



and not the alternative quinoïdal formula,



suggested by Bernthsen.

A. H.

Diphenylene Ketone and Pseudodiphenylene Ketone. By WILHELM KERP (*Ber.*, 1896, **29**, 228—233).—The author has investigated the red compound (pseudophenylene ketone) obtained, together with phenylene ketone, on distilling calcium diphenate (Fittig, *Annalen*, **166**, 373; **193**, 117; Schmidt and Schultz, *ibid.*, **207**, 345). The distillate forms a yellowish-red, crystalline mass of the formula $\text{C}_{12}\text{H}_8\cdot\text{CO}$. The two compounds may be separated by means of dilute alcohol; the red compound crystallises from its ethereal solution in dark red, compact crystals, melts at 85°, and has the same percentage composition as diphenylene ketone (m. p. 83—84°). Both have the same molecular weight, and the pseudo-ketone can readily be converted into the ordinary ketone either by exposure to direct sunlight for several hours, or by treatment with boiling dilute alcohol, steam, or warm sodium ethoxide. In all these decompositions, however, a second red compound is formed, but only in very small quantities; it is still solid at 250°, and is insoluble in alcohol, ether, acids, and alkalis. If heated with alcohol at 300°, the pseudo-ketone is converted into fluorene alcohol. Both the ketone and pseudo-ketone yield the same fluorene alcohol on reduction; they also give the same oximes, and on fusing with potash the same phenylbenzoic acid; these results are, beyond doubt, due to the conversion of the pseudo-ketone into the ordinary ketone.

On treatment with zinc chloride, the oxime, which melts at 195°

(Spiegler, *Abstr.*, 1884, 1182, 192°), yields phenanthridone (Pictet, *Chem. Zeit.*, 1894, 1822), and on reduction is converted into *diphenyl-enemethylamine*, $C_{12}H_{13} \cdot CH \cdot NH_2$; the latter crystallises in colourless needles, melts at 161°, and is moderately soluble in warm water. Ammonium formate reduces both ketones, yielding a mixture of hydrocarbons, among which are, probably, diphenyl and fluorene. According to Schultz (*Annalen*, 203, 103), the ordinary ketone yields a mononitro-derivative when treated with cold, fuming, nitric acid and a dinitro-derivative (m. p. 290°) with warm acid; the author shows that the pseudo-ketone with ice cold nitric acid yields a dinitro-derivative, $\begin{matrix} NO_2 \cdot C_6H_3 \\ NO_2 \cdot C_6H_3 \end{matrix} > CO$, which crystallises in small, yellowish needles, melts at 310°, and is insoluble in most solvents.

J. J. S.

Hydroxybenzylideneacetophenone. (Phenyl Orthohydroxystyryl Ketone). By HERMANN BABLICH and STANISLAUS VON KOSTANECKI (*Ber.*, 1896, 29, 233—236).—*Orthohydroxybenzylideneacetophenone* is best obtained by dissolving salicylaldehyde (1 part) and acetophenone (1 part) in alcohol (6 parts), and then treating with sodium hydroxide (1 part) dissolved in a small quantity of water. After 24 hours, the mixture is poured into water, when orthohydroxybenzylidenediacetophenone (see next page) is thrown down; orthohydroxybenzylideneacetophenone remains in solution as its sodium salt, and may be precipitated on the addition of acid; after thoroughly washing, and recrystallising from alcohol, it forms yellow plates, and melts and decomposes at 153—155°. It dissolves in dilute sodium hydroxide, yielding a yellowish-red solution, and, on adding concentrated alkali to this, the sodium salt separates in the form of orange-coloured needles.

The *acetyl derivative*, $OAc \cdot C_6H_4 \cdot CH : CH \cdot C(=O)Ph$, crystallises in small plates, and melts at 68—69°; when dissolved in chloroform, it readily takes up two atoms of bromine, forming *orthacetoxymethylideneacetophenone dibromide*, which is sparingly soluble in alcohol, crystallises in colourless prisms, and melts at 134—135°.

Metahydroxybenzylideneacetophenone crystallises in colourless plates, melts at 159—160°, and is readily soluble in alcohol, benzene, and chloroform, somewhat more sparingly in carbon bisulphide; its *acetyl derivative* melts at 102—103°, and the *dibromide* of the latter at 170—171°. The dibromide can be reconverted into metacetoxymethylideneacetophenone by treatment with copper powder.

Parahydroxybenzylideneacetophenone forms yellowish crystals, melts at 182—183.5°, and dissolves in dilute alkali, yielding a deep yellow solution. Its *acetyl derivative* melts at 129—131°, and the *dibromide* of this at 148°.

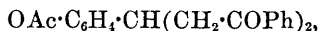
J. J. S.

Phenyl α -Coumaryl Ketone. By STANISLAUS VON KOSTANECKI and JOSEF TAMBOR (*Ber.*, 1896, 29, 237—239).—When orthacetoxymethylideneacetophenone dibromide (see preceding abstract) is dissolved in alcohol, the warm solution treated with strong potash solution, and then poured into water, a crystalline precipitate is obtained. This has the composition $C_{15}H_{10}O_2$, distils at 360° without

decomposition, melts at 91° , and dissolves in concentrated sulphuric acid, yielding a yellow, non-fluorescent solution; when fused with potash, it yields coumarone and benzoic acid, $C_{15}H_{10}O_2 + H_2O = C_8H_6O + C_6H_5\cdot COOH$, its constitution is, therefore, that of *phenyl α -coumaryl ketone*, $C_6H_5\cdot\langle\overset{O}{\underset{||}{CH}}\rangle\cdot C\cdot CPh$.

Paratolyl orthohydroxystyryl ketone, $OH\cdot C_6H_4\cdot CH\cdot CH\cdot CO\cdot C_6H_4Me$, may be obtained from salicylaldehyde and methyl paratolyl ketone in the same way as orthohydroxybenzylidene acetophenone from salicylaldehyde and acetophenone (see preceding abstract); it forms yellowish plates, melts at 152° , and is soluble in alkalis and concentrated sulphuric acid. Its *acetyl derivative* melts at 112° , and the dibromide of this at 136 — 137° . The latter compound, when dissolved in alcohol and treated with concentrated potash, yields *paratolyl α -coumaryl ketone*, $C_6H_4\cdot\langle\overset{O}{\underset{||}{CH}}\rangle\cdot C\cdot CO\cdot C_6H_4Me$; this melts at 96° , and yields coumarone and paratoluic acid when fused with potash. J. J. S.

Action of Aldehydes on Ketones. By ARNOLD CORNELSON and STANISLAUS VON KOSTANECKI (*Ber.*, 1896, **29**, 240—244; compare Schmidt, *Abstr.*, 1881, 573, Claisen and Ponder, *Abstr.*, 1884, 1166).—In the condensation of salicylaldehyde with acetone or with acetophenone, it is necessary to use a much more concentrated solution of sodium hydroxide than in the usual condensations of aldehydes with ketones. With acetophenone and salicylaldehyde, besides the orthohydroxybenzylideneacetophenone (compare Bablich and Kostanecki, preceding page), the authors have obtained a second compound which crystallises from alcohol in colourless needles, and is quite insoluble in alcohol, the amount formed increasing with the amount of alkali used in the condensation. It can also be obtained by the action of acetophenone (1 mol.) on orthohydroxybenzylideneacetophenone in the presence of alkali, and is, beyond doubt, *orthohydroxybenzylidenediacetophenone*, $OH\cdot C_6H_4\cdot CH(CH_2\cdot CPh)_2$. It is best prepared by the action of salicylaldehyde (1 part) on acetophenone (2 parts) dissolved in alcohol (10 parts), and then adding a solution of 2 parts of sodium hydroxide in 2 parts of water. After recrystallisation from alcohol, it forms thin prisms, which melt at 131° ; it is readily soluble in alcohol, benzene, and chloroform, but insoluble in alkalis. When boiled with an alkali, it is decomposed into acetophenone and salicylaldehyde. Its *acetyl derivative*,



crystallises in colourless needles, and melts at 83 — 84° .

Orthohydroxybenzylidenebismethylparatolyl ketone,



was obtained as a bye-product in the preparation of paratolyl hydroxystyryl ketone (compare Kostanecki and Tambor, preceding abstract). It crystallises in colourless prisms, and melts at 131 — 132° ; its *acetyl derivative* melts at 95° .

Bromorthohydroxybenzylidenediacetophenone,

is formed as a bye-product in the preparation of bromorthohydroxybenzylideneacetophenone (compare Kostanecki and Oppelt, following abstract); it crystallises in colourless needles, and melts at 158—159°; its *acetyl derivative* melts at 107°. J. J. S.

Derivatives of Orthohydroxybenzylideneacetophenone (Phenyl Orthohydroxystyryl Ketone). By STANISLAUS VON KOSTANECKI and EUGEN OPPELT (*Ber.*, 1896, **29**, 244—249).—5 : 2-*Bromohydroxybenzylidenediacetophenone*, $\text{OH} \cdot \text{C}_6\text{H}_3\text{Br} \cdot \text{CH} : \text{CH} \cdot \text{COPh}$, is obtained by the action of bromosalicylaldehyde (8 parts) on acetophenone (5 parts) in the presence of an alkali. A small quantity of the corresponding diacetophenone is formed at the same time (compare preceding abstract). It crystallises from its alcoholic solution in yellowish plates, melts and decomposes at 168°, and is soluble in both alkalis and strong sulphuric acid. The *sodium salt* is readily soluble in water, but, on the addition of more alkali, separates out in the form of glistening, red needles. The *acetyl derivative*, obtained by the action of acetic anhydride and anhydrous sodium acetate, forms glistening needles, melts at 133·5—135°, and yields a *dibromide* which melts at 158—160°.

5 : 2-*Bromethoxybenzylidenediacetophenone*, $\text{OEt} \cdot \text{C}_6\text{H}_3\text{Br} \cdot \text{CH} : \text{CH} \cdot \text{COPh}$, may be obtained by boiling an alcoholic solution of the bromohydroxy-compound with ethylic iodide and potassium hydroxide; it may also be obtained from *bromethoxybenzylidenediacetophenone dibromide*, by treating it with a paste of freshly precipitated metallic copper, but is best prepared from the ethylic ether of salicylic acid and acetophenone under the influence of an alkali. It forms yellowish needles, melts at 98—100°, and is readily soluble in warm alcohol. The dibromide may be obtained either by the addition of two atoms of bromine to the ketone, or by the action of bromine on a solution of the crude ethylic ether of orthohydroxybenzylidenediacetophenone in carbon bisulphide. It crystallises in plates, and melts at 165°.

Orthobromophenyl α-coumaryl ketone, $\text{C}_6\text{H}_3\text{Br} < \overset{\text{O}}{\text{CH}} > \text{C} \cdot \text{COPh}$, is obtained when the bromacetoxymethylidenediacetophenone dibromide is suspended in warm alcohol and then treated with concentrated alkali. It crystallises in yellowish needles, and melts at 136—138°.

J. J. S.

Action of Diphenylene Di-isocyanate on Amido-compounds. By H. LLOYD SNAPE (*Chem. News*, 1896, **73**, 37).—When diphenylene dicyanate, obtained by heating benzidine hydrochloride in a current of phosgene gas, is treated in ethereal solution with gaseous ammonia, it yields diphenylenedicarbamide (H. Schiff, *Abstr.*, 1878, 669); whilst, if an ethereal solution of aniline is used, diphenyldiphenylenedicarbamide is formed, identical with that produced from benzidine and phenylic isocyanate (B. Kühn, *Abstr.*, 1885, 979).

D. A. L.

Diphenyldiphenylene-ethylene. By VICTOR KAUFMANN (*Ber.*, 1896, **29**, 73—76).—*Diphenyldiphenylene-ethylene*, $\begin{matrix} \text{C}_6\text{H}_4 \\ | \\ \text{C}:\text{CPh}_2 \\ | \\ \text{C}_6\text{H}_4 \end{matrix}$, is obtained by heating benzophenone chloride and fluorene in molecular proportion at 320—330° for 5—10 minutes; it melts at 229·5°, and crystallises from benzene in colourless leaflets or needles containing the solvent. Reduction of the amylic alcohol solution with sodium amalgam gives rise to *diphenyldiphenylene-ethane*, which crystallises from benzene in leaflets containing 2 mols. of the solvent; it melts at 217—218°. The *picrate* of diphenyldiphenylene-ethylene crystallises from benzene in yellow needles, and melts at 198°.

M. O. F.

Behaviour of Stilbene Dibromide and of Tolane Dibromide with Sodium Benzenesulphinate and Sodium Phenylmercaptide. By ROBERT OTTO (*J. pr. Chem.*, 1896, [2], **53**, 1—19; compare *Abstr.*, 1895, i, 286, 485).—Neither stilbene dibromide nor the corresponding tolane derivative is converted into a sulphone by sodium benzenesulphinate; instead, stilbene dibromide yields stilbene, and β -tolane dibromide yields tolane; tolane and benzil were obtained when α -tolane dibromide was employed. Stilbene and tolane are the products of the action of sodium phenylmercaptide on the aforesaid dibromides.

A. G. B.

Connection between Colour and Constitution in the Triphenylmethane Dyes. By WILHELM VAUBEL (*J. pr. Chem.*, 1896, [2], **53**, 47—48; compare *Abstr.*, 1895, i, 55—56).—The author defends his views concerning the relation of the colour of triphenylmethane dyes and their constitution against the criticism of Richard Meyer in the *Jahrbuch der Chemie*, 1894.

A. G. B.

Hydrocarbons of High Molecular Weight produced by the action of Sodium on Bromobenzene. By MAX WEILER (*Ber.*, 1896, **29**, 115—118; compare this vol., i, 237).—The formation of hydrocarbons of high molecular weight appears to be a normal accompaniment of the action of sodium on brominated aromatic hydrocarbons. The product of the action of sodium on bromobenzene yields a series of compounds which boil above 342°, and of which the molecular weight exceeds 200. A number of crystalline substances has been isolated from the various fractions, but no attempt has yet been made to ascertain the constitution of the products.

A. H.

1:2:3-Dihydroxynaphthoic acid. By RICHARD MÖHLAU and FELIX KRIEBEL (*Ber.*, 1895, **28**, 3089—3096; compare *Abstr.*, 1894, i, 138).—1-Naphthaleneazo-2-hydroxy-3-naphthoic acid forms deep red crystals with a greenish-yellow surface lustre, and decomposes at 182°. 1:2:3-amidohydroxynaphthoic acid forms yellow, rhombic prisms, and decomposes at 205·5°; it can also be obtained by reducing von Kostanecki's 1:2:3-nitrosohydroxynaphthoic acid (*Abstr.*, 1894, i, 91) with stannous chloride. 1:2:3-Dihydroxynaphthoic acid melts and decomposes at 220·5° (not at 207°); its yellow *ethylic* and *methylic* salts melt respectively at 84—84·5° and at 95—96° (for

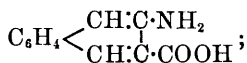
the latter substance compare Gradenwitz, *Abstr.*, 1894, i, 605). When this acid is oxidised with nitric acid of sp. gr. 1.2, it yields 1:2-naphthaquinone-3-carboxylic acid, which crystallises in orange-red monoclinic prisms, and decomposes at 154°; its methylic salt, prepared by oxidation of the corresponding dihydroxy salt, is orange-red, and begins to decompose at 121°, melting at 139—140° (compare Gradenwitz, *loc. cit.*).

C. F. B.

2:3-Amidonaphthoic acid. By RICHARD MÖHLAU (*Ber.*, 1895, 28, 3096—3099; compare *Abstr.*, 1894, i, 138).—This acid is best obtained by heating the sodium salt of the corresponding hydroxy-acid with ammonia in an autoclave at 260—280°; it melts at 214°, (not at 211—212°); the colourless 2-acetamido-derivative melts at 238°, the yellow *methylic salt* at 115—115.5. When a mixture of 2:3-amidonaphthoic and 2:3-hydroxynaphthoic acids with ammonia and zinc chloride is heated at 260—280°, a yellow *dinaphthacridone*, $C_{10}H_6 < \begin{smallmatrix} CO \\ NH \end{smallmatrix} > C_{10}H_6$, melting above 300°, is formed. C. F. B.

Constitution of 2:3-Hydroxynaphthoic acid and its Derivatives. By RICHARD MÖHLAU (*Ber.*, 1895, 28, 3100—3101).—2:3-Hydroxynaphthoic acid is coloured and so are its salts, but when the hydroxylic hydrogen is replaced, colourless compounds are formed. The same is true of the hydroxy-, amido-, and sulphonic derivatives of this acid. The colourless compounds may be regarded as derived from the true hydroxy-acid, $C_6H_4 < \begin{smallmatrix} CH:C\cdot OH \\ CH:C\cdot COOH \end{smallmatrix}$; the coloured ones from the desmotropic isomeride, $C_6H_4 < \begin{smallmatrix} CH_2\cdot CO \\ CH:C\cdot COOH \end{smallmatrix}$.

In the same way, the colourless salts of 2:3-amidonaphthoic acid are to be regarded as derived from the normal acid,



the acid itself and its salts, being coloured yellow, from the desmotropic form, $C_6H_4 < \begin{smallmatrix} CH_2\cdot C\cdot NH \\ CH:C\cdot COOH \end{smallmatrix}$ or $C_6H_4 < \begin{smallmatrix} CH_2\cdot C\cdot NH_2 \\ CH:C\cdot CO \end{smallmatrix} > O$.

C. F. B.

Constitution of 2:3-Hydroxynaphthoic acid. By MARTIN SCHÖPFF (*Ber.*, 1896, 29, 265—270).—Möhlau has recently suggested (preceding abstract) that 2:3-hydroxynaphthoic acid is really a keto-derivative [$CH_2 : CO : COOH = 1 : 2 : 3$]; the author reached the same conclusion some time ago, chiefly from a study of the action of phenylhydrazine on the acid. When heated at 130—140°, they combine, ammonia, water, and *phenylnaphthylcarbazolecarboxylic acid*, $C_{17}H_{11}NO_2$, being formed; the latter crystallises in yellowish-green needles, melts at 325°, and is very sparingly soluble. The *ethylic salt* crystallises in yellow needles, melting at 175°. The *sodium salt* is deposited in silvery, lustrous plates, and becomes yellow at 100°. The *barium*, *magnesium*, and *calcium salts* are yellow and sparingly soluble. The *acetyl derivative* is crystalline, insoluble in alkali, and

remains unmelted at 350°. *Phenylnaphthylcarbazole* is formed by distilling the acid with zinc dust in a current of hydrogen; it crystallises from light petroleum, melts at 120°, and, in solution, has a blue fluorescence; a pine splinter, treated with the carbazole and then with hydrogen chloride, is coloured violet. The *picrate* is crystalline. The *nitroso*-derivative crystallises in small, yellow needles, melts at 132°, gives Liebermann's reaction, and produces a green coloration with concentrated sulphuric acid. The *acetyl* derivative crystallises in silvery, lustrous plates, and melts at 142°. The *benzoyl* derivative is deposited in slender, colourless needles, melting at 170°. The reaction between phenylhydrazine and the naphthoic acid probably takes place in two stages, a hydrazone, $\text{COOH} \cdot \text{C}_{10}\text{H}_7 \cdot \text{N} \cdot \text{NHPh}$, being first formed, and then the carbazolecarboxylic acid, $\begin{array}{c} \text{CH} \cdot \text{C}_6\text{H}_4 \cdot \text{C} \cdot \text{C}_6\text{H}_4 \\ \parallel \quad \parallel \\ \text{C}(\text{COOH}) \cdot \text{C} \cdot \text{NH} \end{array}$.
J. B. T.

Some 1:2'-Derivatives of Naphthalene. By PAUL FRIEDLAENDER and S. ZINBERG (*Ber.*, 1896, **29**, 37—42).—The *sodium hydrogen* and *barium hydrogen salts*, both with $6\text{H}_2\text{O}$, of hydroxydisulphonaphthoic acid $[\text{OH} : \text{COOH} : (\text{SO}_3\text{H})_2 = 1 : 2 : 4 : 2']$ (König, *Abstr.*, 1889, 719) are described. When the acid is fused with sodium hydroxide at 220—240°, it is converted into 1:2':4-*dihydroxy-sulpho-2-naphthoic acid*, the *sodium hydrogen*, and *acid aniline salts* of which were prepared; heating with 50 per cent. sulphuric acid at 140° converts this acid into 1:2'-*dihydroxy-2-naphthoic acid*, which melts and decomposes at 217°, and the *barium salt* of which crystallises with $4\text{H}_2\text{O}$. The latter acid, when boiled with aniline, yields 1:2'-*dihydroxynaphthalene* (Emmert, *Abstr.*, 1888, 57), melting at 175°; concentrated aqueous ammonia converts it at 200—210° into 1:2'-*naphthylenediamine*; at 170—180° into 2':1-*amidonaphthol* (*Abstr.*, 1892, 1234), the *acetyl derivative* of which melts at 210—211°. The isomeric 1:2'-*amidonaphthol* was prepared by heating 1:2'-*naphthylaminesulphonic acid* with sodium hydroxide at 250—260°; it forms pale, brownish needles, and decomposes above 200°; its *acetyl derivative* melts at 165°.
C. F. B.

Menthol. By ERNST JÜNGER and A. KLAGES (*Ber.*, 1896, **29**, 314—318).—In order to establish the formula $\begin{array}{c} \text{CH}_2 \cdot \text{CHMe} \cdot \text{CH}_2 \\ \text{CH}_2 \cdot \text{CHPr}^\beta \cdot \text{CH} \cdot \text{OH} \end{array}$ for menthol (compare *Abstr.*, 1893, i, 359), the authors have converted menthone into dichlorohexahydrocymene, and by elimination of hydrogen chloride obtained chlorotetrahydrocymene, which probably has the constitution $\text{CHMe} < \begin{array}{c} \text{CH}_2 \cdot \text{CCl} \\ \text{CH}_2 \cdot \text{CH}_2 \end{array} > \text{CPr}^\beta$; treatment with bromine and quinoline converts this substance into 3-chlorodihydrocymene, from which 3-chlorocymene is obtained, the chlorine atom occupying the position originally assumed by the hydroxyl group in menthol. In order to identify the cymene derivative thus obtained, the two chlorocymenes have been prepared and characterised.

2-*Chlorocymene* is produced by the chlorination of cymene obtained from camphor; it boils at 117.5° under a pressure of 35 mm., and at

214—216° under atmospheric pressure. The sp. gr. = 1·017, and the refractive index $n_D = 1·51118$ at 17°.

2-Chlorocymene-5-sulphonic acid crystallises from benzene in colourless needles, and melts at 135—136°; the *barium* salt crystallises in leaflets which contain water, and the *chloride*, *amide*, and *anilide* melt at 68—69°, 191—192°, and 181° respectively.

3-Chlorocymene is obtained by the action of phosphorus pentachloride on thymol; it boils at 214°, has sp. gr. = 1·018, and the refractive index $n_D = 1·51796$. The *sulphonamide* crystallises from dilute alcohol in nacreous leaflets, and melts at 168°; the *barium* salt of the sulphonic acid crystallises in needles, and contains 4H₂O.

Chlorotetrahydrocymene, C₁₀H₁₇Cl, is produced by the action of phosphoric chloride on menthone (Abstr., 1892, 867), and quinoline converts its bromo-derivative into *chlorodihydrocymene*, C₁₀H₁₅Cl, which boils at 112° under a pressure of 35 mm., and 212° under atmospheric pressure; this substance has the sp. gr. = 0·990, and the refractive index $n_D = 1·49712$. Treatment of chlorodihydrocymene with bromine (1 mol.), and distillation of the product with quinoline, yields 3-chlorocymene, in every respect identical with the substance already described.

Hexahydrocymene, which is readily produced by the addition of sodium to an alcoholic solution of chlorohexahydrocymene (menthylic chloride), is identical with menthonaphthene, described by Berkenheim (Abstr., 1892, 866), and also with the menthane of Wagner (Abstr., 1894, i, 469).

M. O. F.

Orientation in the Terpene Series: Carone and Pinene. By ADOLF VON BAEYER (*Ber.*, 1896, 29, 3—26; compare Abstr., 1895, i, 549).—The evidence afforded by Wagner (Abstr., 1894, i, 469), and more recently by Wallach (Abstr., 1895, i, 547), in favour of representing terpineol by the formula $\text{CMe} \begin{smallmatrix} \text{CH} \cdot \text{CH}_2 \\ \text{CH}_2 \cdot \text{CH}_2 \end{smallmatrix} > \text{CH} \cdot \text{CMe}_2 \cdot \text{OH}$, has demanded a re-modelling of the author's system of orientation in regard to almost all members of the terpene series excepting those of the terpinolene group. Whilst admitting the accuracy of Wagner's formulæ for terpineol, terpin, limonene, carvone, and dihydrocarvone, Tiemann and Semmler regard pinene as having the constitution

$\text{CH} \begin{smallmatrix} \text{CH}_2 - \text{CH} \\ \text{CH}_2 \\ \text{CMe}_2 \cdot \text{CHMe} \end{smallmatrix} > \text{C}$ (Abstr., 1895, i, 428), basing this hypothesis

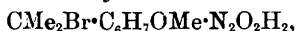
on the behaviour of pinonic acid towards oxidising agents (Abstr., 1895, i, 477). The author, however, has oxidised pinene in the manner indicated by these investigators, and obtained pinonic acid in a form which, although having the empirical formula C₁₀H₁₆O₃, and boiling at the temperature observed by them, becomes crystalline very readily, and, on oxidation with alkali hypobromite, yields a dibasic acid of the composition C₉H₁₄O₄, to which he refers as pinic acid. This behaviour is not in agreement with the foregoing expression, and pinene must, therefore, be represented by the formula

$\text{CH} \begin{smallmatrix} \text{CH}_2 - \text{CH} \\ \text{CH}_2 < \\ \text{CMe} - \text{CH} \end{smallmatrix} > \text{CMe}_2$, already advocated by Wagner (*loc. cit.*).

The production of hydrobromodihydrocarvone and hydroxytetrahydrocarvone, by the addition of the elements of hydrogen bromide and of water to carone, meets with explanation if the constitution of the latter substance is expressed by the formula $\begin{array}{c} \text{CHMe} \cdot \text{CO} \cdot \text{CH} \\ | \qquad \qquad | \\ \text{CH}_2 - \text{CH}_2 \cdot \text{CH} \end{array} > \text{CMe}_2$ (compare Abstr., 1895, i, 551); this view removes the author's objection to Bredt's formula for camphor, which he now regards as more probable than the expression advocated by Tiemann (Abstr., 1895, i, 428).

The conversion of carvone, limonene, terpineol, pinene, nitrosopinene, and isocarvoxime into hydrochlorocarvoxime by a method described in the present paper, is regarded as justifying the classification of these substances in one natural group.

It has been already mentioned that hydroxytetrahydrocarvone is formed by the addition of the elements of water to carone. Caronebisnitrosylic acid, also, when dissolved in alcohol and submitted to the action of a current of steam, yields 8-hydroxytetrahydrocarvonebisnitrosylic acid, $\text{OH} \cdot \text{CMe}_2 \cdot \text{CH} < \begin{array}{c} \text{CH}_2 \cdot \text{CH}_2 \\ | \qquad | \\ \text{CH}_2 - \text{CO} \end{array} > \text{CMe} \cdot \text{N}_2\text{O}_2\text{H}_2$, which crystallises from dilute methylic alcohol in rhombic plates, and melts and evolves gas at 184° . Glacial acetic acid saturated with hydrogen bromide converts it into bromotetrahydrocarvonebisnitrosylic acid,



which also crystallises in rhombic plates, and melts and decomposes at 130° ; treatment with alcoholic potash regenerates caronebisnitrosylic acid. *Hydroxycarone* is obtained from bisnitrosocarone dichloride and hydrobromodihydrocarvone dibromide by the action of caustic soda; it boils at $125\text{--}135^\circ$ under a pressure of 20 mm., and forms a crystalline sodium derivative. Hydroxycarone and *ketoterpine*, obtained by agitation with sulphuric acid, will be more fully described. Oxidation of eucarvone with potassium permanganate has led to the formation of asymmetric dimethylsuccinic acid.

When the α - and β -modifications of *d*-limonene nitrosochloride are treated with alcoholic hydrogen chloride, active hydrochlorocarvoxime is produced; the inactive modification is obtained, however, from hydrochlorodipentene nitrosochloride, terpineol nitrosochloride, pinene nitrosochloride, and nitrosopinene. The active hydrobromocarvoxime is produced when α -dextrolimonene nitrosochloride is treated with ethereal hydrogen bromide, whilst pinene nitrosochloride and terpineol nitrosochloride yield the inactive modification; eucarvone, however, is indifferent towards this agent.

On oxidising pinene, according to the method adopted by Tiemann and Semmler (Abstr., 1895, i, 477), the chief product obtained by the author is α -pinonic acid, $\text{C}_{10}\text{H}_{16}\text{O}_3$, which melts at $103\text{--}105^\circ$, and boils at $180\text{--}187^\circ$ under a pressure of 14 mm.; the oxime crystallises in large, transparent plates or prisms, and melts at 150° , whilst the *phenylhydrazone* crystallises from dilute alcohol in lustrous, colourless leaflets, which melt and decompose below 100° . This result is not in agreement with the observations of the above-men-

tioned investigators, who obtained liquid pinonic acid, which boils at the same temperature as the solid modification, and yields two isomeric oximes, melting at 125° and 160° respectively. A crystalline acid which the author calls *nopic acid* is another product of the oxidation of pinene, but it is not formed when the pure hydrocarbon is employed; it is isomeric with pinonic acid, but, unlike this substance, it is not ketonic. Nopic acid melts at 125° , and the sodium salt is sparingly soluble in water.

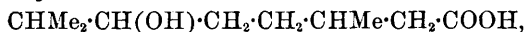
Tiemann and Semmler have observed that pinonic acid is indifferent towards alkali hypobromite (*loc. cit.*); α -pinonic acid, however, is readily oxidised by this agent, yielding *pinic acid*, $C_9H_{14}O_4$, which crystallises from water in long prisms, and melts at 101 – 102.5° . Pinic acid is dibasic, but does not form an anhydride under the influence of boiling acetic chloride; the solution is slowly oxidised by potassium permanganate on the water bath, but is indifferent towards it at the ordinary temperature. Hydrobromic acid has no action on pinic acid at 100° , and the aqueous solution is optically inactive.

M. O. F.

Orientation in the Terpene Series. Menthone and Tetrahydrocarvone. By ADOLF VON BAEYER [and EUGEN OEHLER] (*Ber.*, 1896, 29, 27–37; compare *Abstr.*, 1894, i, 522, and 1895, i, 549).—2:6-Dimethyl-3-oximidoctanoic acid, the open chain acid derived from nitrosomenthone by the addition of the elements of water, melts at 103° (compare *loc. cit.*). 2:6-Dimethyloctan-3-onoic acid, obtained by treating it with boiling dilute acids, boils at 186 – 187° under a pressure of 20 mm.; the *semicarbazone* crystallises in prisms and melts at 152° .

Isobutyrylmethylketopentamethylene (1:4-methylisobutoylcyclopentane-3-one), $CHMe \cdot \begin{matrix} CH_2 \cdot CO \\ | \\ CH_2 \cdot CH \cdot CO \cdot CHMe_2 \end{matrix}$, is formed when the ethylic salt of the foregoing acid is heated with sodium and xylene for three hours at 120 – 130° ; it is a colourless oil, boiling at 115 – 116° under a pressure of 25 mm., and develops a red coloration in alcoholic solution with ferric chloride; the *copper* derivative crystallises in bright green, silky needles, and *compounds* are also formed with sodium hydrogen sulphite and ammonia. The *dioxime* crystallises in small needles, and melts at 144° . On heating the diketone with aqueous potash, the ketonic acid is regenerated.

2:6-Dimethyloctan-3-oloic acid,



is obtained by heating 2:6-dimethyloctan-3-onoic acid with absolute alcohol and sodium; the *silver* salt crystallises in lustrous leaflets, and the *lactone* boils at 155 – 165° under a pressure of 25 mm. On oxidising the acid with potassium permanganate, β -methyladipic acid is formed.

5-Isopropylheptan-2-onoic acid, $CH_3 \cdot CO \cdot CH_2 \cdot CH_2 \cdot CHPr^{\beta} \cdot CH_2 \cdot COOH$, is obtained by the action of amyl nitrite and hydrochloric acid on tetrahydrocarvone, the product being hydrolysed with dilute sulphuric acid; it forms colourless crystals, melting at 40° , and boils at

192° under a pressure of 20 mm. The *semicarbazone* melts at 152—153°, and the *oxime* at 75—78°; the *phenylhydrazone* crystallises in golden needles and melts at 102°, and the *ethylic* salt boils at 143—146° under a pressure of 12 mm.

Acetylpropylketopentamethylene (1 : 4-acetylisopropylcyclopentan-2-one), $\text{CHAc} < \begin{smallmatrix} \text{CO}-\text{CH}_2 \\ \text{CH}_2 \cdot \text{CHPr}^a \end{smallmatrix} >$, is obtained from the foregoing ethylic salt by means of sodium and xylene; it is a sweet, colourless oil, which boils at 130—132° under a pressure of 25 mm. The *copper* derivative crystallises in light green needles, and the *dioxime* melts at 165°; hydrolysis of the diketone gives rise to the original acid.

When bisnitrosotetrahydrocarvone is treated with ethereal hydrogen chloride, tetrahydrocarvonebisnitrosylic acid is formed, crystallising in leaflets, which melt and decompose at 82°; the *oxime* of bisnitrosotetrahydrocarvone is also produced, and melts at 75—77°. In preparing the bisnitrosylic acid, a chlorinated ketone is formed, which yields a new *terpenone*, $\text{C}_{10}\text{H}_{16}\text{O}$, when treated with sodium acetate and acetic acid; the *semicarbazone* melts at 222—223°.

Isopropylheptanonoic acid is also formed when tetrahydrocarvone is gently oxidised with potassium permanganate; more vigorous action gives rise to isopropylsuccinic acid. M. O. F.

The Terpenes and Camphor. By FERDINAND TIEMANN (*Ber.*, 1896, 29, 119—131).—The author reviews the course of his recent investigations, and discusses the changes attending the conversion of camphoroxime into campholenitrile. In the light of von Baeyer's work (this vol., i, 246), the oily pinonic acid obtained by Tiemann and Semmler (*Abstr.*, 1895, i, 478) on oxidising pinene is regarded as a mixture of isomerides; a similar mixture is produced when α -dihydroxydihydrocampholenic acid (m. p. 144°) is distilled, and this fact is considered favourable to the pinene formula already advocated by Tiemann and Semmler (*loc. cit.*). M. O. F.

Bromo-derivatives of the Camphor Series. By ANGELO ANGELI and E. RIMINI (*Gazzetta*, 1895, 25, ii, 162—164; compare *Abstr.*, 1895, i, 382).—The authors ascribe to ordinary bromocamphor, to the isomeride melting at 113°, obtained by the action of hydrogen bromide on camphenone, and to monobromocamphenone, the following constitutions respectively: $\text{C}_7\text{H}_{13} < \begin{smallmatrix} \text{CH} \\ \text{CO} \end{smallmatrix} > \text{CHBr}$, $\text{C}_7\text{H}_{13} < \begin{smallmatrix} \text{CBr} \\ \text{CO} \end{smallmatrix} > \text{CH}_2$, $\text{C}_7\text{H}_{13} < \begin{smallmatrix} \text{C} \\ \text{CO} \end{smallmatrix} = > \text{CBr}$. These constitutions are in agreement with Bredt's formula for camphor. W. J. P.

Ledum-camphor. By EDVARD I. HJELT (*Ber.*, 1895, 28, 3087—3089).—The stearoptene contained in oil of wild marsh rosemary, obtained from the leaves of *Ledum palustre* (*Abstr.*, 1882, 346), has the molecular formula $\text{C}_{15}\text{H}_{26}\text{O}$; Rizza's analysis had already indicated this. It is thus a camphor of the sesquiterpene series; it melts at 104—105° and boils at 282—283°; it dissolves in alcohol to the extent of 10·4

per cent. at 17.5° , and the solution is feebly dextrorotatory, $[\alpha]_D = 7.98$; it is a poison, affecting the central nervous system. Warming with dilute sulphuric acid on the water bath suffices to make it lose water and yield the sesquiterpene *ledene*, $C_{15}H_{24}$, which is an oil boiling at 255° , and rapidly acquiring a greenish tinge. On account of the ease with which the camphor loses water, it is difficult to get the hydroxyl group to react; neither benzoic chloride nor phenylic isocyanate form derivatives, but the *chloride*, $C_{15}H_{25}Cl$, can be obtained as a yellowish oil by the action of successive small quantities of phosphorus pentachloride on a solution of the camphor in light petroleum; heating with quinoline converts this chloride into *ledene*.

C. F. B.

Ammoniacum. By H. Luz (*Arch. Pharm.*, 1895, **233**, 540—550).—The sample examined contained 4.5 per cent. of water, 69 per cent. of resin, 22.7 per cent. of substances soluble in water, and 3.5 per cent. of substances, other than resin, insoluble in water. A considerable amount of salicylic acid was present, but no aldehydes or terpenes. Normal butyric and valeric acids were also present, largely in combination with a resin alcohol, *ammoresinotannol*, $C_{18}H_{30}O_3$, a chocolate-brown, tasteless, and odourless powder, insoluble in water, but soluble in alkalis and acids. Ammoresinotannol is oxidised by nitric acid to styphnic acid. The resin consists essentially of ammoresinotannol salicylate. The *acetyl* derivative, $C_{18}H_{28}AcO_3$, is a brown powder, soluble in acetone, &c. The *benzoyl* derivative is similar. The gum of gum ammoniacum appears to contain calcium arabinat.

JN. W.

Conversion of Acetylacetone into Pyrroline Derivatives.

By CARLO U. ZANETTI (*Real. Accad., Lincei*, 1893, i, 324—327).—

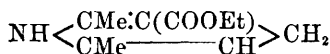
3:5-Diacetyl-2:4-dimethylpyrroline, $NH \begin{smallmatrix} \text{CMc} \cdot \text{C} \cdot \text{Ac} \\ \text{C} \cdot \text{Ac} \cdot \text{CMc} \end{smallmatrix}$, is formed on adding potassium nitrite to a cooled acetic acid solution of acetylacetone, and then reducing the product with zinc dust; on filtering and neutralising with sodium carbonate, the base separates, and is ultimately obtained in colourless, flattened needles, melting at 136° . It is soluble in most organic solvents, and is a very feeble base; the *aurochloride*, $C_{10}H_{13}NO_2 \cdot HAuCl_4$, melts at 120 — 130° with previous decomposition, and is decomposed by water. On heating the base with potash and benzaldehyde, it yields 3:5-dicinnamoyl-2:4-dimethylpyrroline, $C_{24}H_{21}NO_2$, which crystallises in nodular groups of small needles, melting at 215 — 216° .

Nitrosoacetylacetone, $(COMe)_2C:NOH$, the intermediate product in the preparation of the above pyrroline, may be isolated by adding sulphuric acid to a potash solution of acetylacetone containing potassium nitrite, and then extracting with ether; on evaporating the ethereal solution and recrystallising, it is obtained in flattened needles or scales, melting at 75° . It is soluble in water, alcohol, or ethylic acetate, but only sparingly so in benzene or petroleum.

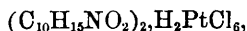
On heating sodioacetylacetone, suspended in ether, with iodine, a substance, $C_{10}H_{11}O_4$, is obtained, which melts at 186 — 187° , and is possibly symmetrical tetracetylene.

W. J. P.

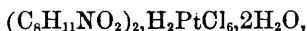
Synthesis of Pyridine Derivatives by the Action of Ethylic Acetoacetate on Aldehydes in Presence of Ammonia. By ROBERT SCHIFF and P. PROSIO (*Gazzetta*, 1895, **25**, ii, 65—90).—On gradually adding alcoholic ammonia to a mixture of ethylic acetoacetate and commercial formaldehyde solution, heat is generated, and Griess and Harrow's ethylic dihydrolutidinedicarboxylate, melting at 176—183° (Abstr., 1888, 1313), is slowly deposited; the action proceeds in accordance with the equation $2C_6H_{10}O_3 + H \cdot COH + NH_3 = C_{13}H_{19}NO_4 + 3H_2O$, and a 95 per cent. yield is obtained. The same substance is deposited immediately on adding the requisite amount of a hydrochloric acid solution of formaldehyde to a mixture of ethylic acetoacetate and alcoholic ammonia, so that the action proceeds both in acid and in alkaline solutions; the ethereal salt has neither acid nor basic properties, and, when heated with hydrochloric acid, yields ethylic lutidinedicarboxylate, melting at 72°, but no hydrogen is evolved as stated by Griess and Harrow (*loc. cit.*), the effervescence being due to carbonic anhydride and ethylic chloride. The same conversion may be effected by saturating an absolute alcoholic solution of ethylic dihydrolutidinedicarboxylate with dry hydrogen chloride, evaporating the alcohol, and adding sodium carbonate, when ethylic lutidinedicarboxylate separates. The alkaline mother liquor contains *ethylic 2 : 6-dimethyl-1 : 4-dihydropyridine-3-carboxylate*,



it is extracted by ether, and is ultimately obtained as a yellowish oil of coniine-like odour, which distils unchanged at 235°, and is more soluble in cold than in hot water. The *platinochloride*,



crystallises in yellow needles melting at 140°, and the compound with mercuric chloride, $C_{10}H_{15}NO_2, HgCl_2$, is a yellow powder insoluble in water. The salt is readily hydrolysed by potash yielding the corresponding acid, of which the *hydrochloride*, $C_8H_{11}NO_2, HCl$, forms small glassy crystals, whilst the *platinochloride*,



crystallises in small red prisms, which lose their water at 120°.

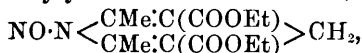
On heating ethylic dihydrolutidinedicarboxylate with alcoholic potash, ammonia is evolved, and, on adding water and extracting with ether, Knoevenagel's tetrahydroketotoluene (Abstr., 1895, i, 48), which boils at 192—197°, is obtained; it is doubtless formed by isomeric change occurring in a substance of the constitution



which should be first produced from the dicarboxylate. The alkaline mother liquors, when exactly neutralised, deposit *lutidinedicarboxylic acid*, $C_8H_9NO_4$; this crystallises from boiling water in thin, white needles having a very high melting point, and is only sparingly soluble in alcohol or ether. The same acid may be prepared from

the sodium salt obtained by the action of sodium ethoxide on ethylic lutidinedicarboxylate.

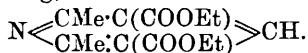
Nitric acid (sp. gr. 1.36—1.40) dissolves ethylic dihydrolutidinedicarboxylate with slight rise of temperature, and, after neutralisation, the product yields ethylic lutidinedicarboxylate crystallising in compact scales, which melt at 72° and become electrified by friction. On leaving the dihydrolutidinedicarboxylate in contact with fuming hydrochloric acid, and then neutralising with sodium carbonate, a substance is deposited which crystallises in long, lustrous needles melting at 71—72°, but which does not become electrified by friction. On recrystallisation from boiling solvents, however, this labile substance becomes converted into the above stable modification, which is easily electrified; if, however, instead of crystallising the precipitate obtained by adding carbonate, it is merely washed and dried, it is found to be an *imido-base* isomeric with the original so-called ethylic dihydrolutidinedicarboxylate, and melts at 58—60°. This base, *ethylic isodihydrolutidinedicarboxylate*, has the constitution $\text{NH} \langle \text{CMe:C(COOEt)} \rangle \text{CH}_2$, and is very readily oxidised by exposure to the air or by heating with alcohol, giving ethylic lutidinedicarboxylate. It readily yields a *nitroso-derivative*,



crystallising with $\frac{1}{2}\text{H}_2\text{O}$ in yellow needles which melt at 52°, and lose water at 115°; by reduction with stannous chloride and ammonia, it yields another *base*, $\text{C}_{13}\text{H}_{19}\text{NO}_4$, which crystallises with $\frac{1}{2}\text{H}_2\text{O}$, and melts at 88°.

Ethylic lutidinedicarboxylate gives a nitroso-derivative, but has basic properties, and thus gives a *picrate*, $\text{C}_{13}\text{H}_{17}\text{NO}_4 \cdot \text{C}_6\text{H}_2(\text{NO}_2)_3 \cdot \text{OH}$, which separates in long, yellow crystals melting at 118—119°; the original ethylic salt and its isomeric are found to have double the normal molecular weight by the boiling point method.

The authors conclude that the original ethylic dihydrolutidinedicarboxylate melting at 176—183° is wrongly named; it contains no pyridine nucleus, but is an open chain compound of the constitution $\text{CH}_2 \cdot \text{C(COOEt)} \cdot \text{CMe} \cdot \text{N} \cdot \text{CMe} \cdot \text{CH} \cdot \text{COOEt}$. This compound, by the migration of one hydrogen atom, readily yields the closed chain imido-base, which is termed ethylic isodihydrolutidinedicarboxylate, and has the constitution $\text{NH} \langle \text{CMe:C(COOEt)} \rangle \text{CH}_2$. This compound is readily oxidised on exposure to air, yielding the labile form of ethylic lutidinedicarboxylate melting at 72°, to which the constitution $\text{N} \langle \text{CMe:C(COOEt)} \rangle \text{CH}$ must be assigned; this unstable form, on recrystallisation, then assumes the stable form which becomes electric on rubbing, and has the constitution



W. J. P.

Dicarboxylic acids of the Piperidine Bases. By WILHELM KOENIGS (*Ber.*, 1895, 28, 3148—3150; compare the following ab-

stract).—A number of the dicarboxylic acids of the piperidine bases have been synthetically prepared in order to throw light on the constitution of cincholeuaponic acid, which is obtained by the oxidation of the quinine alkaloids. In addition to those described in the succeeding abstract, the following compounds have been examined. The *hydrochloride of hexahydrocinchomeronic acid* melts and decomposes at 237°, whilst the *hydrochloride of hexahydrolepidinic acid* melts and decomposes at 222°. No attempt has yet been made to resolve these acids into optically active constituents. A. H.

Reduction of Quinolinic acid. By EMIL BESTHORN (*Ber.*, 1895, 28, 3151—3160; compare the foregoing abstract).—When quinolinic acid, in dilute alcoholic solution, is reduced with sodium amalgam, it yields the lactone of δ -hydroxybutane- $\alpha\gamma\delta$ -tricarboxylic acid (Perlmutter, *Abstr.*, 1893, i, 176); whilst, if it is dissolved in boiling amyl alcohol and treated with metallic sodium, it is converted into nipecotinic acid, carbonic anhydride being lost at the temperature of the experiment. On the other hand, again, reduction with metallic sodium and ethylic alcohol yields *hexahydroquinolinic acid*, $\begin{matrix} \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH} \cdot \text{COOH} \\ \text{CH}_2 \cdot \text{NH} \cdot \text{CH} \cdot \text{COOH} \end{matrix}$; the product obtained is a mixture of two geometrically isomeric acids, which can be separated by means of their nitroso-compounds. Which of these acids is the *cis*-form, and which the *cis-trans*-form, has not yet been definitely decided. (1) One of the nitroso-acids is only sparingly soluble in cold water; it is, however, readily soluble in hot water, crystallises in large compact crystals, and melts and decomposes at 154°. The *barium salt* is very readily soluble in water, whilst the *silver salt* is only sparingly soluble. This nitroso-acid may be resolved into two optically active constituents by the fractional crystallisation of its strychnine salt. The new acids thus obtained, and the hexahydroquinolinic acids prepared from them, scarcely differ from the racemoid forms, except in optical activity; they will shortly be more fully described. The *hydrochloride of hexahydroquinolinic acid*, obtained by the action of concentrated hydrochloric acid on the nitroso-acid, forms slender, white needles, melting and decomposing at 221°, whilst the *aurochloride* melts at 185°. The free acid separates from water in compact, white crystals melting at 253°; it is scarcely soluble in alcohol and other organic solvents. The *hydrochloride of methylic hexahydroquinolinic acid* melts and decomposes at 166—167°. (2) The more readily soluble nitrosohexahydroquinolinic acid was not itself isolated, but when decomposed with hydrochloric acid it yields the *hydrochloride of hexahydroquinolinic acid*, which melts at 239°, and, unlike the isomeric salt just described, is only sparingly soluble in concentrated hydrochloric acid. The *aurochloride* melts and decomposes at 195°. The free acid melts at 227°, and is much more readily soluble in water than its isomeride; it has hitherto only been obtained as a glassy mass. The hydrochloride melting at 239° is completely converted into the isomeric salt, melting at 221°, when it is dissolved in amyl alcohol, treated with sodium, isolated in the form of a nitroso-acid, and finally re-obtained

from this compound by the action of hydrochloric acid. The *hydrochloride of methylic hexahydroquinolinic acid* melts and decomposes at 189–190°, whilst the corresponding *ethylic derivative* melts and decomposes at 204–205°.

Hexahydroquinolinic acid acts towards bases as a monobasic acid, whilst the nitroso-acid is dibasic.

It has so far proved impossible to resolve the acid melting at 227° into optically active constituents, although since the groups combined with its two asymmetric carbon atoms are dissimilar, it should, like the isomeride, be capable of such resolution. A. H.

Optically Active 2-Pipecolines and "Isopipecoline." By WILHELM MARCKWALD (*Ber.*, 1896, **29**, 43–51).—Inactive synthetical 2-pipecoline can be separated into its active components by adding *d*-tartaric acid and concentrating, when *d*-2-pipecoline *d*-hydrogen tartrate crystallises out. From the mother liquor, the base is set free, and then made to crystallise with *l*-tartaric acid, when *l*-2-pipecoline *l*-hydrogen tartrate crystallises out. This process is repeated, *d*- and *l*-tartaric acid being used alternately to effect crystallisation; an almost quantitative separation can thus be effected. These two hydrogen tartrates both have the composition $C_6H_{13}N, C_4H_6O_6 + 2H_2O$; both melt at 65–66° or, when anhydrous, at 111–112°, and both form monoclinic crystals, which are enantiomorphous but otherwise identical; $a : b : c = 1.1698 : 1 : 1.7477$; $\beta = 81^\circ 20'$. The hydrochlorides, cadmiiodides, platinochlorides, aurochlorides, picrates, and dithiocarbamates, $(C_6H_{13}N \cdot CS \cdot SH \cdot C_6H_{13}N)$, melt respectively at 190° (205°), 147° (131°), 194° (186°), 131–132° (118–119°), 116–117° (127–128°), 141–142° (126°); the numbers given in brackets are the melting points of the corresponding salts of inactive 2-pipecoline. *l*-2-Pipecoline, liberated from its *l*-hydrogen tartrate prepared as above, has a rotation $\alpha_D = -32.0^\circ$, in a tube 100 mm. long, and is of the same magnitude as that of the *d*-isomeride; it had not hitherto been obtained pure.

d-2-Pipecoline *l*-hydrogen tartrate and *l*-2-pipecoline *d*-hydrogen tartrate both crystallise with H_2O ; both melt at 45–46°, and when anhydrous at 126°.

2-Pipecoline hydrogen racemate can be prepared from inactive 2-pipecoline and racemic acid, or from *d*-2-pipecoline *d*-hydrogen tartrate and *l*-2-pipecoline *l*-hydrogen tartrate, or from *d*-2-pipecoline *l*-hydrogen tartrate and *l*-2-pipecoline *d*-hydrogen tartrate. It crystallises with H_2O in monoclinic crystals; $a : b : c = 2.670 : 1 : 1.368$; $\beta = 85^\circ 46.5'$; and melts at 85°.

Ladenburg's statement (*Abstr.*, 1894, 306) that a new substance, isopipecoline, is obtained when *d*-2-pipecoline hydrochloride is distilled with zinc dust, is incorrect; what really happens is a partial conversion of *d*- into *l*-pipecoline. If *l*-pipecoline chloride is boiled in an atmosphere of hydrogen, it undergoes a partial conversion into the *d*-isomeride. C. F. B.

α -Naphthylpiperidine. By JULIUS ABEL (*Ber.*, 1895, **28**, 3106–3111; compare *Abstr.*, 1890, 1002).— α -Naphthylpiperidine (*loc. cit.*)

is formed when piperidine (8.5 grams) is heated with α -naphthol (14.4 grams) at 250–260° for 4–5 hours; it is a pale yellow oil which boils at 215° under a pressure of 35 mm., and exhibits a beautiful blue fluorescence. The hydrochloride forms colourless crystals melting at 178–179°; the *aurochloride* melts at 128–129°, and the *picrate* crystallises in yellow needles, and melts at 179–180°; the *ferrocyanide* separates in colourless crystals, and the *mercurichloride* is amorphous.

Tetrahydro- α -naphthylpiperidine is obtained by adding a solution of α -naphthylpiperidine (15 grams) in dry amyl alcohol (200 grams) to molten sodium (25 grams); it is a pale, yellow oil which boils at 218° under a pressure of 63 mm., and reduces cold, alcoholic silver nitrate. The *hydrochloride* crystallises with difficulty, and the *mercurichloride* is amorphous, the *ferrocyanide* being obtained in white crystals; the *platinochloride* forms small, lustrous crystals, melting at 190–192°, and the *aurochloride* crystallises in golden-yellow leaflets, and melts at 148–149°. Oxidation of tetrahydro- α -naphthylpiperidine with potassium permanganate in presence of alkali gives rise to adipic acid.

M. O. F.

2 : 3- and 3 : 4-Dibromoquinoline. By ADOLPH CLAUS [and, in part, KARL LODHOLZ and FRITZ HIRSCHBRUNN] (*J. pr. Chem.*, 1896, [2], 53, 25–38).—2 : 3-Dibromoquinoline melts at 68°, and 3 : 4-dibromoquinoline at 135°, not 95° and 124° respectively as previously stated (Abstr., 1890, 172).

3 : 4-Dibromoquinoline *platinochloride* and *methiodide* are described.

The bromination of 3 : 4-dibromoquinoline hydrobromide in chloroform solution produces 3 : 4 : 3'-tribromoquinoline, which melts at 149°, and was formerly described as 3 : 4 : 4'-tribromoquinoline (Abstr., 1894, i, 473); the *platinochloride* is described.

3 : 4 : 1-Dibromonitroquinoline is the sole product of the nitration of 3 : 4-dibromoquinoline in the usual manner; it sublimes in the form of lustrous needles and melts at 152°: its basic properties are very feeble; the *platinochloride* is described.

2 : 3-Dibromoquinoline differs from the 3 : 4-derivative in its volatility in steam at atmospheric pressure; its *platinochloride* and *methiodide* are described.

2 : 3 : 1-Dibromonitroquinoline is the more abundant product when 2 : 3-dibromoquinoline is nitrated without warming; it sublimes in nearly colourless, lustrous crystals, melts at 191°, and dissolves freely in ether and chloroform, but only sparingly in alcohol, and not at all in water; the *platinochloride* is described, but no *methiodide* could be obtained. The corresponding *amido*-derivative crystallises in colourless, slender needles, and melts at 68°.

1 : 2 : 3-Tribromoquinoline is prepared from 2 : 3 : 1-dibromamidoquinoline through the diazo-reaction; it crystallises in colourless needles, melts at 84°, and does not easily sublime; the *hydrochloride* and *platinochloride* are described.

2 : 3 : 4-Dibromonitroquinoline is the more abundant product of the nitration of 2 : 3-dibromoquinoline when the temperature is raised; it is more soluble in alcohol than is the accompanying 2 : 3 : 1-derivative,

and crystallises and sublimes in colourless needles melting at 165° . The *methiodide* is easily prepared (compare the 2 : 3 : 1-derivative), and melts and decomposes at about 250 — 252° . The *platinochloride* is described. The corresponding *amido*-derivative crystallises in small, colourless needles, and melts at 119° .

2 : 3 : 4-*Tribromoquinoline*, prepared like the 1 : 2 : 3-derivative, crystallises and sublimes in colourless needles, and melts at 124° .

2 : 3 : 3'-*Tribromoquinoline* is prepared by the Claus-Collischonn method (bromination of the appropriate dibromoquinoline hydrobromide in chloroform solution) from 2 : 3-dibromoquinoline; it sublimes in lustrous, colourless prisms, and melts at 116.5° . The *platinochloride* and the *methiodide* are described. A. G. B.

Action of Bromine on Para- and Ortho-Hydroxyquinoline.

By ADOLPH CLAUS and HANS HOWITZ (*J. pr. Chem.*, 1895, [2], 52, 532—547).—The authors have previously stated that the red dibromide obtained by adding bromine (2 atoms) to 4 : 3-bromhydroxyquinoline hydrobromide suspended in chloroform decomposes when exposed to air, with loss of hydrogen bromide and formation of a dibromo-3-hydroxyquinoline. This statement is incorrect; the compound merely loses the two atoms of bromine, the original 4 : 3-bromhydroxyquinoline being left.

1 (? 2) : 4 : 3' : 3-*Tribromhydroxyquinoline* is obtained when the foregoing dibromide, or a mixture of 4 : 3-bromhydroxyquinoline with bromine (2 mols.) is heated in a sealed tube at 200 — 250° . It crystallises in slender, silky, colourless needles, melts at 257° , and dissolves very sparingly in mineral acids and in alcohol, but freely in warm glacial acetic acid. Oxidation by potassium permanganate converts it into 3-bromopyridinedicarboxylic acid and 3-bromonicotinic acid; this settles, to some extent, its orientation.

2 : 4 : 1-*Dibromhydroxyquinoline hydrobromide* separates as a yellow crystalline precipitate when bromo-1-hydroxyquinoline is brominated in chloroform solution; it melts at 250° , and sublimes slowly in the form of slender needles; when warmed with water, it yields the corresponding *base*, which separates in crystalline flocks, and melts at 196° . When this dibromhydroxyquinoline is brominated in chloroform, the *dibromide* of the hydrobromide is precipitated in yellow needles or prisms, which melt at 160 — 170° , the molten mass rapidly losing bromine; in water, this compound loses hydrogen bromide without loss of its bromine. By heating the dibromide in a sealed tube at 250° , 2 : 4 : 3' : 1-*tribromhydroxyquinoline* may be obtained; it is at first a yellow powder, but sublimes in colourless needles, which melt at 169 — 170° ; oxidation with permanganate converts it into 3-bromopyridinedicarboxylic acid. The authors regard this tribromhydroxyquinoline as identical with that obtained by Claus and Heermann by the action of phosphorus pentabromide on 1 : 4-hydroxyquinolinesulphonic acid (*Abstr.*, 1891, 82). A. G. B.

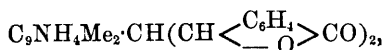
3-Ethoxyquinoline. By C. GRIMAUZ (*Compt. rend.*, 1895, 121, 749—751).—3-*Ethoxyquinoline* or *quinethoil*, $C_9H_7 \cdot OEt$, is an oily

liquid obtained by the action of glycerol and sulphuric acid on ethyl phenyl ether. It boils at 290—292° without decomposing, and with inorganic acids forms crystalline salts, the solutions of which show fluorescence similar to that of quinine. The nitrate crystallises in needles melting at 165°. The salts with organic acids are decomposed by water. The *nitro*-derivative is not obtained by the action of nitric acid alone, but is prepared by adding nitric acid to a solution of the base in sulphuric acid, and treating the product (the nitrate of the *nitro*-derivative) with potassium or sodium hydroxide, or by adding the nitrate of the base to sulphuric acid, diluting with water, and precipitating with ammonia. It melts at 110°, crystallises in needles or in flat rhomboïdal prisms according to the conditions, and has feebly basic properties. The *amido*-derivative crystallises from boiling water in sulphur-yellow prisms containing 1 mol. H₂O, and, when anhydrous, melts at 110°. With acids, it forms red monacid salts, which dye silk a pale yellow; the diacid salts are colourless. The *diazo*-derivative yields coloured compounds.

3-Ethoxyquinoline is without any effect even in the simplest intermittent fevers, and has no antipyretic properties. C. H. B.

Action of Orthoaldehydic acids on Quinaldine in Presence of Zinc Chloride. By K. NENCKI (*Ber.*, 1896, 29, 187—190; compare M. Nencki (*Abstr.*, 1894, i, 518).—*Phthalidylquinaldine*,

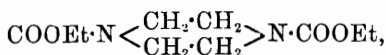
$C_9NH_5 \cdot CH_2 \cdot CH < \text{---} \text{C}_6H_4 > CO$, is prepared by heating aqueous solution of phthaldehydic acid and quinaldine, in molecular proportion, with zinc chloride during eight hours; the product is extracted with dilute hydrochloric acid, and the solution treated with soda; the precipitate crystallises from alcohol in colourless needles, and melts at 104°. The *platinochloride*, $(C_{18}H_{13}O_2N)_2 \cdot H_2PtCl_6$, is yellow and crystalline; the *aurochloride* has also been prepared. *Diphthalidylquinaldine*, $C_9NH_5 \cdot CH(CH < \text{---} \text{C}_6H_4 > CO)_2$, is obtained, along with the preceding compound, and can be separated from it by means of its insolubility in hydrochloric acid; it crystallises from absolute alcohol in needles, and melts at 192°. The combined yield is 50 per cent. of the theoretical, including 10 per cent. of the diphthalidyl. *Phthalidyl-dimethylquinaldine*, $C_9NH_4Me_2 \cdot CH_2 \cdot CH < \text{---} \text{C}_6H_4 > CO$, [$Me_2 = 1 : 3$], prepared from phthaldehydic acid and dimethylquinaldine, crystallises in colourless needles, melts at 116°, and is insoluble in dilute alkali. *Diphthalidyl-dimethylquinaldine*,



is colourless, crystalline, melts at 224°, and is formed in small quantity together with the preceding compound. *Opianyldimethylquinaldine*, $C_9NH_4Me_2 \cdot CH_2 \cdot CH < \text{---} \text{C}_6H_2(OMe)_2 > CO$ [$Me_2 = 1 : 3$], prepared from opianic acid and 1:3-dimethylquinaldine, crystallises in colourless, slender needles, melts at 132°, and dissolves in alkali

(30 per cent.) only after prolonged boiling. The *platinochloride*, $(C_{28}H_{27}O_4N)_2 \cdot H_2PtCl_6$, forms yellow crystals. The formulæ given to the above compounds accord with their insolubility in alkali, and in their formation the aldehydic acids react as hydroxyphthalides (compare Liebermann, this vol., i, 232). J. B. T.

Derivatives of Piperazine. By G. ROSDALSKY (*J. pr. Chem.*, 1896, [2], 53, 19—24).—*Ethyllic piperazine-1 : 4-dicarboxylate*,



is prepared by shaking an aqueous solution of piperazine with ethylic chlorocarbonate and potash, and extracting with ether; it crystallises in needles, melts at 42° , boils at 315° , and dissolves in the usual solvents.

Piperazine-1 : 4-dicarboxylamide, $C_4N_2H_8(CONH_2)_2$, is precipitated when cold concentrated solutions of piperazine hydrochloride and potassium cyanate are mixed; it crystallises from hot water in lustrous, rhombic crystals, and from boiling alcohol in short prisms; it is insoluble in ether and benzene. The corresponding *anilide*, $C_4N_2H_8(CO \cdot NHPh)_2$, is an amorphous, insoluble substance, precipitated by adding phenylic isocyanate to an aqueous solution of piperazine.

Tri-carbonylpiperazine, $(C_4N_2H_8 \cdot CO)_3$, separates as an amorphous precipitate when carbonyl chloride is passed into an alkaline solution of piperazine; it is insoluble in the usual solvents.

Tri-phthalylpiperazine, $(C_4N_2H_8 < \begin{smallmatrix} CO \\ CO \end{smallmatrix} > C_6H_4)_3$, is an amorphous precipitate, formed when phthalic chloride is added to an alkaline solution of piperazine.

Piperazine-1 : 4-diphenylsulphone, $C_4N_2H_8(SO_2Ph)_2$, from benzene sulphonic chloride and piperazine, is an amorphous precipitate.

1 : 4-Methylenepiperazine, $C_4N_2H_8 \cdot CH_2$, from piperazine and formaldehyde, is a white precipitate, insoluble in water, alcohol, ether, benzene, and caustic soda, and decomposed by dilute acids into the parent substances.

Piperazine ethylic oxalate, $C_4N_2H_{10}(COOH \cdot COOEt)_2$, is obtained by heating hydrated piperazine with ethylic oxalate in alcoholic solution; it crystallises from water in thick prisms, and melts at 181° . Alcoholic ammonia converts this compound into *piperazine oxamate*, $C_4N_2H_{10}(COOH \cdot CONH_2)_2$, which crystallises in monoclinic tables.

1 : 4-Diethoxalylpiperazine, $C_4N_2H_8(CO \cdot COOEt)_2$, is obtained when anhydrous piperazine and ethylic oxalate are heated together in absolute alcohol; it is separated from other products by boiling benzene, and melts at 115° (compare Schmidt and Wichmann, *Abstr.*, 1892, 210).

The compound, $C_{16}H_{26}N_2O_4$, is formed when ethylic acetoacetate and piperazine are warmed together; it crystallises in white, felted needles, melts at 140° , and dissolves sparingly in ether and benzene, but not in water.

Carbonic anhydride produces a crystalline precipitate, $C_5H_{10}N_2O_2$, in an alcoholic solution of piperazine. A. G. B.

Steric Hindrances to Chemical Reactions. By PAVEL IW. PETRENKO-KRITSCHENKO (*Ber.*, 1895, **28**, 3203—3207; compare this vol., i, 134). The ethereal salt, formed by the action of phenylhydrazine on ethylic methylacetonedicarboxylate, is shown to have the constitution, $CO < \begin{smallmatrix} NPh \cdot N \\ CHMe \end{smallmatrix} > C \cdot CH_2 \cdot COOEt$, since the acid formed on hydrolysis loses carbonic anhydride when heated, and yields Knorr's dimethylphenylpyrazolone, $CO < \begin{smallmatrix} NPh \cdot N \\ CHMe \end{smallmatrix} > CMe$, on distillation in a vacuum.

The author criticises some of the conclusions drawn by V. Meyer (this vol., i, 145) from his work on the etherification of triphenylacetic and triphenylacrylic acids. In contradistinction to V. Meyer, the author regards the phenyl-group as equivalent to a primary, rather than to a tertiary, radicle. This conclusion is supported by reference to the author's own work, and also to that of Meyer and of Lean.

Victor Meyer, in an appended note, states that he does not agree with all the author's conclusions. J. J. S.

Aromatic Homologues of Ethylenediamine. By FRANZ FEIST and HUGO ARNSTEIN (*Ber.*, 1895, **28**, 3167—3181; compare *Abstr.*, 1895, i, 274).—The dibenzoyl compound of phenylethylenediamine, when heated in a current of hydrogen chloride at 240° , is converted into 2:4-diphenyldihydroglyoxaline, $NH < \begin{smallmatrix} CPh \cdot N \\ CH_2 \cdot CHPh \end{smallmatrix} >$, which crystallises in hard, colourless prisms, melting at 78° . Diacetophenylethylenediamine crystallises in snow-white plates, melting at 152° . The thiocarbamate of the base, $CHPh < \begin{smallmatrix} NH \cdot CS \\ CH_2 \cdot NH_2 \cdot SH \end{smallmatrix} >$, melts and decomposes at 97° .

Phenylethylenethiocarbamide crystallises in white plates, and melts at 184° . The diamine does not yield a well characterised product with ethylic oxalate or benzaldehyde, but readily reacts with benzile, forming 2:3:5-triphenyl-5:6-dihydropyrazine, $N < \begin{smallmatrix} CPh - CPh \\ CH_2 \cdot CHPh \end{smallmatrix} > N$, which crystallises in bronze-coloured plates, melting at 149° . Phenylphenanthrapyrazine, $\begin{smallmatrix} CPh \cdot N : C \cdot C_6H_4 \\ | \\ CH - N : C \cdot C_6H_4 \end{smallmatrix}$, crystallises in silky, yellow needles, melting at 190° . Phenyl- β -naphthapyrazine melts at 187° .

Diphenylethylenediamine forms a bitartrate, which crystallises in fascicular groups of needles, melting with decomposition at 165 — 166° . The fractional crystallisation of this salt from warm water resulted in the separation of its two optically active components, the dextro-rotatory base forming the more readily soluble salt. The two components have not yet been completely separated. An attempt to convert the racemic form of the base into hydrobenzoin by means of

the action of sodium nitrite, resulted in the production of a very small amount of isohydrobenzoïn, which must therefore be the racemic form of this compound. Small amounts of isodiphenylhydroxyethylamine and of diphenylacetaldehyde were also obtained in the same reaction.

Diacetophenylethylenediamine is a white powder, which melts above 360°. The *dibenzoyl-compound* melts at 287°. *Trinitrodibenzodiphenylethylenediamine* may be obtained by direct nitration, and forms a yellow powder, melting at 137° with decomposition. The dibenzoyl-compound is remarkably stable, and can only be converted into an anhydro-base by hydrogen chloride at 260°. 2:4:5-Triphenyl-4:5-dihydroglyoxaline, $\text{CPh} \begin{array}{c} \text{NH} \cdot \text{CHPh} \\ \diagdown \quad \diagup \\ \text{N} - \text{CHPh} \end{array}$, prepared as just described, is isomeric with amarine, and melts at 175°. 2:4:5-Methyldiphenyl-4:5-dihydroglyoxaline, $\begin{array}{c} \text{CHPh} \cdot \text{NH} \\ \diagdown \quad \diagup \\ \text{CHPh} - \text{N} \end{array} > \text{CMe}$, may be prepared in a similar manner, and melts at 162°. *Diphenylethylenedicarbamide* crystallises in colourless needles, and melts above 360°. The *dithiocarbamide* melts and decomposes at 192°. *Diphenylethylenediamine thiocarbamate* is a light yellow, crystalline powder, which melts at 132°. *Diphenylethylenethiocarbamide* is obtained by the distillation of the foregoing compound, and is a white, granular powder, melting at 183—184°.

The base unites with two molecular proportions of ethylic oxalate, forming an additive compound, which melts at 164°. When heated with ethylic oxalate, on the other hand, a compound of the formula, $\begin{array}{c} \text{CHPh} \cdot \text{NH} \\ \diagdown \quad \diagup \\ \text{CHPh} \cdot \text{NH} \end{array} > \text{C} \begin{array}{c} \text{OEt} \\ \diagdown \quad \diagup \\ \text{COOEt} \end{array}$, is obtained in white crystals, melting and decomposing at 242°. The *dibenzylidene derivative* of the base melts at 152°. Diphenylethylenediamine reacts with benzil to form tetraphenylpyrazine. With phenanthraquinone, it yields the compound, 2:3-diphenylphenanthrapyrazine, $\begin{array}{c} \text{CPh} \cdot \text{N} \cdot \text{C} \cdot \text{C}_6\text{H}_4 \\ | \quad | \\ \text{CPh} \cdot \text{N} \cdot \text{C} \cdot \text{C}_6\text{H}_4 \end{array}$, which crystallises in slender, light-brown needles, melting at 265°. A. H.

Pyrazolone. By LUDWIG KNORR (*Ber.*, 1896, **29**, 249—259; compare von Rothenberg, *Abstr.*, 1893, i, 180, 367, 428, 611, and 729; 1894, i, 349, 350, and 622; 1895, i, 302, 571, and 686; Ruhemann, *Abstr.*, 1894, i, 476).—The author points out that the pyrazolone described by Ruhemann has properties entirely different from those of the pyrazolone described by von Rothenberg, and as the possibility of isomerism is theoretically impossible, one of the statements must be wrong. The two formulæ given by Ruhemann for pyrazolone and isopyrazolone, the author considers, represent desmotropic forms of the same substance. The author has prepared pyrazolone from hydrazine hydrate and ethylic formylacetate, and finds that it agrees in all its properties with the substance described by Ruhemann, and he therefore concludes that the oily substance (b. p. 156—157°) described by von Rothenberg can only be a solution of pyrazolone, and not the

pure substance, especially as it shows no analogy in its general properties to 1:3-phenylmethyl-5-pyrazolone and 3-methyl-5-pyrazolone, which have been previously prepared.

Pyrazolone, as obtained by the action of hydrazine sulphate on the sodium salt of ethylic formylacetate in the presence of free alkali, crystallises from toluene or xylene in minute needles, begins to sinter at 160°, and melts at 163–164°; it has no odour, is readily soluble in water and alcohol, but only sparingly in ether. It has reducing properties, is coloured reddish-brown by ferric chloride, and is only slightly volatile with steam. When heated, it sublimes, at the same time undergoing decomposition. It is further characterised by possessing both acid and basic properties; solutions of pyrazolone cannot be titrated with litmus as an indicator, since the litmus is turned blue when only about 3/10ths of the theoretical quantity of alkali has been added. An oily and extremely hygroscopic *hydrochloride* may be obtained, but it gives no precipitates with either platinum or gold chloride. In contradistinction to von Rothenberg's compound, it is not decomposed when heated with concentrated hydrochloric acid at 100°.

The sodium salt may be obtained as a solid, hygroscopic residue on evaporating a solution of pyrazolone in the requisite quantity of sodium hydroxide solution. The solution of the sodium salt yields precipitates with silver nitrate, barium chloride, cobalt sulphate, nickel sulphate, copper sulphate, and mercuric chloride solutions.

4-Benzylidenepyrazolone, $C_3N_2H_2O:CHPh$, crystallises in minute, orange coloured needles, and melts at 200°; whereas Rothenberg describes it as a semi-solid mass of a purple-red colour.

4-Isonitrosopyrazolone, $NH < \begin{smallmatrix} CO \cdot C \cdot N \cdot OH \\ N : CH \end{smallmatrix}$, crystallises from its aqueous solutions in long, hair-like needles, or in small, compact, yellow prisms; it melts at 180–181°, and, at the same time, undergoes decomposition. According to von Rothenberg, it crystallises in brown needles and melts at 87°. The *silver salt* forms deep red, felted needles.

The *hydrazone*, $NH < \begin{smallmatrix} CO \cdot C \cdot N \cdot NHPh \\ N = CH \end{smallmatrix}$, crystallises in orange coloured plates, and melts at 196° (Rothenberg gives 185°). The *paratolyl-hydrazone* melts and decomposes at 223° (Rothenberg, 219°). The author thinks that his compounds are identical with those described by von Rothenberg, but that the latter were by no means pure. Pyrazolone, prepared by Ruhemann's method (Trans., 1895, 1008), gives derivatives identical with those described above. J. J. S.

Metallic Double Salts of Antipyrine (Dimethylphenylpyrazolone). By LEOPOLD VAN ITALLIE (*Ned. Tydschr. Pharm.*, 1895, 7, 295–298).—*Antipyrine zinc chloride*, $(C_{11}H_{12}N_2O)_2 \cdot ZnCl_2$.—If aqueous solutions of zinc chloride and antipyrine are mixed in molecular proportion, oily globules are formed, which first become pasty and afterwards crystalline. The crystals are anhydrous, and melt at 155°. The salt is also obtained by slowly evaporating a mixture of zinc chloride

and antipyrine in alcoholic solution, or by mixing this solution with ether.

The corresponding iodide forms well-defined crystals, showing double refraction, and the bromide colourless crystals, moderately soluble in water.

On adding a solution of mercurous nitrate to an alcoholic solution of antipyrine, a greyish-black deposit is obtained, consisting of a compound of antipyrine with both mercurous and mercuric nitrates. The amount of combined mercury is, however, very variable, and there is always a small quantity of metallic mercury in the precipitate.

L. DE K.

Quinacridine. By STEFAN NIEMENTOWSKI (*Ber.*, 1896, **29**, 76—83).—The condensation of phloroglucinol with anthranilic acid yields a derivative of quinacridine, the name given by the author to a base, the structure of which resembles that of anthracene or phenanthrene.

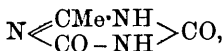
Hydroxyquinacridone, $C_6H_4<\overset{NH}{\underset{CO}{\parallel}}>C_6H(OH)<\overset{NH}{\underset{CO}{\parallel}}>C_6H_4$, is obtained by heating phloroglucinol with anthranilic acid at 150° for 15—20 minutes, and then at 200—230° for 1—2 hours; it remains solid at 370°, becoming black at 410°. This substance is insoluble in the usual organic solvents, but crystallises in minute cubes from phenol and phenylhydrazine; the solution in concentrated sulphuric acid is yellow, and exhibits green fluorescence. The *acetoxyquinacridone* is amorphous, and undergoes no change at 360°. The *trinitro*-derivative is insoluble in organic solvents and dissolves in alkalis; it decomposes and becomes black at 270—280°.

Quinacridine, $C_6H_4<\overset{N-}{\underset{CH}{\parallel}}>C_6H_2<\overset{N-}{\underset{CH}{\parallel}}>C_6H_4$, is formed when hydroxyquinacridone is distilled from zinc dust; it crystallises from benzene in colourless leaflets, and melts at 221°. A *compound*, which is probably an isomeride, is also formed, crystallising from the mother liquor and melting at 213°; it forms a platinochloride, resembling that of acridine, and this base is also produced when hydroxyacridone is submitted to the treatment indicated.

Tetrahydroquinacridine, $C_{20}H_{16}N_2$, is obtained by reducing quinacridine in alcoholic solution with sodium amalgam; it crystallises from benzene in golden-yellow leaflets, and melts at 272°, softening at 255°. Acetic anhydride dissolves it with the production of an intense blood-red solution, which deposits quinacridine on cooling; the solution in boiling benzene is yellow, and exhibits a beautiful, green fluorescence.

M. O. F.

Methyldioxytriazine (Acetoguanamide). By A. OSTROGOVICH (*Annalen*, 1895, **288**, 318—321).—*Methyldioxytriazine*,



identical with acetoguanamide, described by Nencki (*Ber.*, 1876, **9**, 234), is obtained by heating acetylurethane (6 grams) with carb-

amide (2·7 grams) for six hours at 140—150°, ethylic acetate being formed at the same time. The *hydrochloride* crystallises in needles, and the *platinochloride* is yellow; the *silver* derivative is white, and the *lead* derivative is crystalline. Dilute nitric acid converts methyl-dioxytriazine into cyanuric acid, and bromine gives rise to a *tribromo*-derivative, which yields cyanuric acid and bromoform when treated with boiling water. M. O. F.

α : μ -**Dimethyloxazole**. By ADOLF SCHUFTAN (*Ber.*, 1895, **28**, 3070—3071).—This substance, $N \leq \begin{smallmatrix} \text{CMe}\cdot\text{CH} \\ \text{CMe}\cdot\text{O} \end{smallmatrix}$, can be obtained from chloroacetone and acetamide, contrary to Lewy's statement (*Abstr.*, 1888, 1101), by heating them in the proportions of $1\frac{1}{2}$:1 parts by weight for eight hours at 110—120°; much of the acetamide remains unchanged, however. It is a colourless liquid, with an odour like that of pyridine and hardly distinguishable from that of α : μ -dimethylthiazole; it boils at 108°; its *hydrochloride*, *platinochloride* (decomposing at 196°), *aurochloride*, and *mercurochloride* (melting between 82—90°) were prepared. C. F. B.

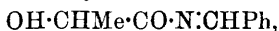
New Synthesis of Oxazoles. By EMIL FISCHER (*Ber.*, 1896, **29**, 205—214).—When hydrogen chloride is passed into a cooled ethereal solution of benzaldehydecyanhydrin and benzaldehyde, the *hydrochloride* of β : μ -diphenyloxazole, $O < \begin{smallmatrix} \text{CPh}\cdot\text{CH} \\ \text{CPh}\cdot\text{N} \end{smallmatrix}$, crystallises out. This melts and decomposes at 160—165°; water decomposes it, precipitating the oxazole, which melts at 74° and boils just above 360°; the *methiodide* melts and decomposes at 196° (corr. 201°), and has the character of a quaternary base. The oxazole, in acetic acid solution, is oxidised by chromic acid to *phenylglyoxyl-benzamide*,



which melts at 142—143° (corr. 146°). When reduced with sodium in boiling alcoholic solution, the oxazole yields *benzylphenylhydroxyethylamine*, $\text{CH}_2\text{Ph}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CHPh}\cdot\text{OH}$, which melts at 100—101° (corr. 104°), and distils without decomposing. The *hydrochloride* of this base melts at 220° (corr. 226°); the *nitrosamine* melts at 93° (corr. 95°), and does not give Liebermann's reaction. The base is reduced by hydriodic acid at 140—150° to *benzylphenylethylamine*, $\text{CH}_2\text{Ph}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CH}_2\text{Ph}$, which boils at 327—328° under 750 mm. pressure; the *hydriodide* melts at 227° (corr. 233°), the *hydrochloride* at 264—266°, and the *sulphate* at 186—187° (corr. 191—192°). This base is more conveniently prepared by reducing with sodium in boiling alcoholic solution the condensation product of benzylamine with phenylacetaldehyde.

β : μ -Diphenyloxazole can also be prepared by warming benzamide with crude phenylbromacetaldehyde, $\text{CHPhBr}\cdot\text{CHO}$. This last is itself obtained by brominating a cooled chloroform solution of phenylacetaldehyde, and distilling off the chloroform in a vacuum; the product can be distilled under 1 mm. pressure.

The cyanhydrins of aliphatic aldehydes do not yield oxazoles in the manner described above. Acetaldehyde cyanhydrin and benzaldehyde, if left in ethereal solution containing 2 per cent. of hydrogen chloride, condense to *benzylidenelactamide*,



which melts at 130—131° (corr. 133—134°).

C. F. B.

Synthesis of Caffeine. By EMIL FISCHER and LORENZ ACH (*Ber.*, 1895, 28, 3135—3143; compare this vol., i, 12).—The synthesis of caffeine is effected by means of the following operations: (1) Production of dimethylbarbituric acid from malonic acid and dimethylcarbamide; (2) conversion of dimethylbarbituric acid into dimethylvioluric acid under the influence of nitrous acid; (3) reduction of dimethylvioluric acid to dimethyluramil, and transformation of the latter into dimethylpseudouric acid by means of potassium cyanate; (4) conversion of dimethylpseudouric acid into γ -dimethyluric acid (*loc. cit.*); (5) formation of chlorotheophylline by the action of phosphorus pentachloride on γ -dimethyluric acid; (6) reduction of chlorotheophylline to theophylline, and conversion of the latter into caffeine.

Chlorotheophylline, $\begin{matrix} \text{NMe}\cdot\text{CCl}\cdot\text{C}\cdot\text{NH} \\ \text{CO}\cdot\text{NMe}\cdot\text{C}=\text{N} \end{matrix} > \text{CO}$, is obtained by heating an intimate mixture of γ -dimethyluric acid, phosphorus pentachloride (2 parts) and phosphorus oxychloride (4 parts) in sealed tubes at 150° for 2½ hours; it crystallises from acetone in aggregates of colourless needles, which melt and decompose about 300°. It is very sparingly soluble in chloroform, but dissolves more freely in acetone, and is readily soluble in hot alcohol; it dissolves in 150 parts of boiling water, forming an acid solution, and is readily soluble in ammonia, alkalis, and concentrated mineral acids. Chlorine water produces the change characteristic of xanthine and its derivatives. The *sodium* and *silver* derivatives crystallise in slender, white needles, the latter substance being insoluble in water, and gradually becoming dark when exposed to light. When chlorotheophylline is reduced with hydriodic acid, theophylline is produced (Kossel, *Abstr.*, 1888, 1114); the action of methylic iodide on the silver derivative gives rise to chlorocaffeine.

Bromotheophylline is formed when a mixture of phosphorus pentabromide and phosphorus oxychloride acts on γ -dimethyluric acid, chlorotheophylline being produced at the same time; it is also obtained by heating theophylline with bromine for four hours at 100° and subsequently at 150°. Bromotheophylline separates from alcohol in colourless crystals, and melts and decomposes at 315—320° (uncorr.); it is very sparingly soluble in hot water, but dissolves readily in ammonia and alkalis. Hydriodic acid readily converts it into theophylline.

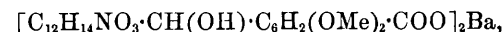
Dimethylbarbituric acid is converted into the sodium derivative of dimethylvioluric acid by adding a concentrated solution of sodium nitrite to an aqueous solution of the acid at 60°; the sodium derivative contains 3H₂O (compare Andreasch, *Abstr.*, 1895, i, 337), which is removed at 115°. Anhydrous dimethylvioluric acid melts at 141°, and

in the hydrated condition at 124° (compare *loc. cit.*, and Techow, Abstr., 1895, i, 84).
M. O. F.

Morphine. By E. VONGERICHTEN (*Ber.*, 1896, **29**, 65—68).—The author considers that there is much evidence to show that morphine must have the nitrogen atom attached directly to a carbon atom of the benzene ring. He explains the decomposition of methylmorphine methohydroxide, when its aqueous solution is evaporated, by the equation $C_{18}H_{20}MeNO_3 \cdot Me \cdot OH = NMe_3 + C_{15}H_{10}O_2 + C_2H_4 + 2H_2O$. The compound $C_{15}H_{10}O_2$ is a phenanthrene derivative, and it yields a *tetrabromo-derivative*, $C_{15}H_6Br_4O_2$, which melts at 290° .

C. F. B.

Synthesis of an Isomeric Narcotine. By CARL T. LIEBERMANN (*Ber.*, 1896, **29**, 183—187).—Opianic acid and hydrocotarnine are mixed in molecular proportion and introduced into sulphuric acid (about 73 per cent.) free from nitrites, the liquid is well cooled, and after 12 hours diluted with ice-cold water, the unaltered opianic acid is removed, and on the addition of soda *isonarcotine*, $C_{22}H_{23}NO_7$, is precipitated; it crystallises from alcohol in colourless needles or prisms, melts at 194° , and is insoluble in alkalis. With pure concentrated sulphuric acid, a carmine coloration is obtained, the production of which may also be used as a test for the presence of opianic acid, cotarnine, or hydrocotarnine. The yield is excellent. When boiled with baryta water, the *salt*,



is formed, from which *isonarcotine* is regenerated by successive treatment with sulphuric acid and soda. The *hydrochloride*, $C_{22}H_{23}NO_7 \cdot HCl + 2H_2O$, is crystalline, readily soluble, and without physiological action on rabbits. The *hydrobromide* is more sparingly soluble than the hydrochloride; the *hydriodide* is practically insoluble in cold water, and, like the *nitrate*, crystallises in colourless needles. The *platinochloride* and *aurochloride* are yellow. Attempts to synthesise narcotine from meconine and cotarnine, or hydrastine from meconine and hydrastinine, and from opianic acid and hydrohydrastinine have hitherto been unsuccessful.

Hydrocotarninephthalide, $C_6H_4 < \begin{array}{c} CO \\ CH(C_{12}H_{14}NO_3) \end{array} > O$, is prepared, in a similar manner to *isonarcotine*, from hydrocotarnine and phthalaldehydic acid; it crystallises from alcohol, melts at 193° , gives a pale yellow coloration with concentrated sulphuric acid, and, in alcoholic solution, has an alkaline reaction. The *platinochloride* is pale yellow and flocculent. The *hydriodide*, $C_{20}H_{19}NO_5 \cdot HI$, crystallises in needles, and, like the *nitrate*, is sparingly soluble.

J. B. T.

Replacement of the Hydroxyl Group of the Cinchona Alkaloids by Hydrogen. By WILHELM KOENIGS (*Ber.*, 1895, **28**, 3143—3148).—When cinchonine chloride is dissolved in dilute sulphuric acid and treated with iron filings, a small amount of cinchene is formed along with *deoxycinchonine*, $C_{19}H_{22}N_2$, in which the chlorine atom of the cinchonine chloride is displaced by hydrogen. The base

melts at 90—92°, and dissolves in alcohol, the solution being strongly dextrorotatory. It is not identical with dihydrocinchene. When heated with hydrobromic acid, additive products alone are formed, whilst with phosphoric acid, a little lepidine is produced. On oxidation with potassium permanganate in acid solution, it does not yield cinchoninic acid, but a product which appears to be derived from deoxycinchotenine, $C_{15}N_{20}N_2O_2$. *Deoxyconchinine*, $C_{20}H_{24}N_2O + 2H_2O$, prepared from conchinine chloride, crystallises in the asymmetric system, and melts at 80—82°. It is readily soluble in 10 per cent. aqueous tartaric acid, and does not yield apoquinine when heated with hydrobromic acid, an additive compound being the sole product. The base is thus sharply distinguished from conchinene, which melts at the same temperature. The alcoholic solution of the base is strongly dextrorotatory, and has a deep violet-blue fluorescence.

A. H.

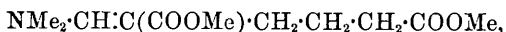
Resolution of Tropinic acid. By RICHARD WILLSTÄTTER (*Ber.*, 1895, 28, 3271—3292; compare this vol., i, 65).—*i*-Tropinic acid was prepared from tropine by Merling's method; the yield is 30—38 per cent., that of *d*-tropinic acid, from ecgonine, is 29 per cent. Both acids, when titrated, give values indicating their monobasicity; phenolphthaleïn was employed as indicator. *Methylic i-tropinate*, $C_8H_{11}NO_4Me_2$, is prepared by the action of hydrogen chloride on tropinic acid and methylic alcohol, and is a colourless, odourless, neutral oil; it boils at 268—272°, and is in part decomposed; potassium permanganate reacts slowly with it; when hydrolysed, tropinic acid is regenerated. The yield is 70—90 per cent. of the acid employed, but it is smaller if hydrogen bromide or sulphuric acid is used. The *aurochloride* is oily. The *picrate* crystallises in small, orange-yellow, quadratic prisms, melts at 121°, and is conveniently used for the purification of the methylic salt.

Methylic d-tropinate resembles the inactive compound; its *picrate* crystallises in long, thin needles melting at 120—121°.

Methylic i-tropinate methiodide, $C_8H_{11}NO_4Me_2, MeI$, is formed only slowly, and crystallises with $\frac{1}{2}H_2O$ from methylic alcohol in highly refractive, long prisms, from water in thin, prismatic aggregates, melting and decomposing at 172°, whilst, from ether, anhydrous, slender, nacreous plates are deposited. The *aurochloride* of the *methochloride* crystallises in thin, slender, golden, lustrous plates, and melts at 116—117°. When treated with silver oxide, the above methiodide

yields a *betaine* derivative,
$$\begin{array}{c} CH_2 \cdot CH_2 \cdot \overset{\overset{|}{COOMe}}{CH} \cdot CO \\ COOMe \cdot \overset{\overset{|}{CH}}{CH} \cdot CH_2 \cdot NMe_2 \cdot O \end{array}$$
, the *aurochloride* of which crystallises in long, orange-yellow needles melting at about 182°. *Dimethylic d-tropinate methiodide* crystallises in colourless plates and needles, which melt and decompose at 177°. The *aurochloride* of the *methochloride* crystallises in microscopic, quadratic plates and needles melting at 114°; the corresponding derivative of the *betaine*, is deposited in slender needles, which melt and decompose at 195°. Hofmann has shown that dimethylpiperylammonium iodide is decomposed by alkali into hydriodic acid and dimethylpiperidine; methylic *i*-tropinate methiodide behaves in a similar manner; when

heated at 70—80° for two minutes with potassium carbonate, it yields *methylic i-methyltropinate*,



which is a faintly coloured, oily liquid with an extremely feeble alkaline reaction; it boils at 280° (corr.), and decomposes in part under the ordinary pressure; potassium permanganate is instantaneously decolorised. The yield is about 90 per cent. of the theoretical. When fused with potash, first at 160°, and finally at 240—250°, it is converted into adipic acid, formic acid, dimethylamine, and, in small quantity, acetic acid. The yield of adipic acid is about 60 per cent. of the theoretical. *Methylic i-* and *d-tropinate* methiodide and *methylic d-methyltropinate* react in the same manner. *Methylic i-methyltropinate* *platinochloride*, $(\text{C}_{11}\text{H}_{10}\text{NO}_4)_2\cdot\text{H}_2\text{PtCl}_6$, crystallises in orange-red, prismatic aggregates, and in well developed, highly refractive needles from water and hydrochloric acid respectively, and melts at 147—148°. The *aurochloride* is oily; the *picrate* is deposited in long, transparent, amber-coloured crystals melting at about 77—78°. *Methylic i-methyltropinate methiodide* crystallises in spherical, aggregated prisms melting at 131—132°; if deposited from alcohol, they contain $\frac{1}{2}\text{H}_2\text{O}$. The *aurochloride* of the *methochloride*,

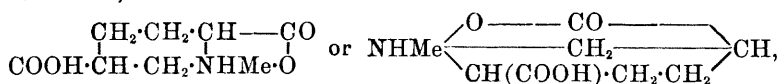


forms well developed golden prisms melting at 118°, whilst the corresponding *monomethylic* derivative, $\text{C}_9\text{H}_{14}\text{MeNO}_4\cdot\text{MeAuCl}_4$, crystallises in sulphur-yellow, prismatic aggregates, which soften at about 100°. *Methylic d-methyltropinate methiodide* resembles the inactive isomeride, and melts at 121—122°.

When *methylic i-* and *d-methyltropinate* methiodides are boiled with soda they yield trimethylamine, *piperylenedicarboxylic acid*, $\text{CH}_2\text{:C(COOH)}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}\cdot\text{COOH}$, and hydriodic acid, whilst a portion is resolved into its constituents; the reaction corresponds with that by which Hofmann prepared piperylene, $\text{CH}_2\text{:CH}\cdot\text{CH}_2\cdot\text{CH}\cdot\text{CH}_2$, from the compound obtained by the complete methylation of piperidine. The acid crystallises from water in long, silky needles and prisms, melts at 169°, decomposes carbonates readily, rapidly decolorises potassium permanganate solution, and is dibasic; the electrolytic conductivity, $K = 0.0116$, $\mu_{\infty} = 354$. The yield is 75 per cent. of the theoretical. The *silver* salt, $\text{C}_7\text{H}_6\text{O}_4\text{Ag}_2$, is deposited in slender, microscopic prisms; under the same conditions, $\Delta^1.2$ -pentenedicarboxylic acid yields a characteristic hydrogen silver salt. The *basic copper* salt is greenish-blue; the *lead* salt white and flocculent; the *zinc* salt is granular; the *cadmium* salt is crystalline. *Tetrabromopiperylenedicarboxylic acid*, $\text{C}_7\text{H}_6\text{O}_4\text{Br}_4$, crystallises from formic acid in colourless prisms, melts and decomposes at 218°, is stable towards potassium permanganate, and is rapidly decomposed by alkalis. The formation of this compound shows that piperylenedicarboxylic acid contains two double linkings, but their position remains undetermined.

Propylic i-tropinate is prepared in the same way as the *methylic* salt, which it resembles in general properties; the *methiodide* is oily;

the *aurochloride* of the *methochloride*, $C_8H_{11}Pr^2NO_4, MeAuCl_4$, crystallises in slender, sulphur-coloured needles, and melts at 103° . When the above methiodide is treated with potassium carbonate, it yields *propylic i-methyltropinate*, the *methiodide* of which crystallises in lustrous, stellate needles and prisms melting at $116-117^\circ$; when it is heated with soda, piperylenedicarboxylic acid and trimethylamine are produced. The formation of the above methylic and propylic tropinate methiodides shows that tropinic acid contains a tertiary nitrogen atom, as indicated by Merling's formula; Ladenburg's formula indicates the presence of a secondary nitrogen atom. The production of adipic acid from methyltropinic acid, described above, is probably preceded by that of formyladipic acid, $OH \cdot CH \cdot C(COOH) \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot COOH$, which is then further hydrolysed to adipic and formic acids. The monobasicity of tropinic acid suggests that it may be a betaine derivative,



but the methylic and propylic salts have not this constitution, since the latter, after complete methylation, yields trimethylamine, and not dimethylpropylamine. J. B. T.

Cactus Alkaloids. II. By ARTHUR HEFFTER (*Ber.*, 1896, **29**, 216-229; compare *Abstr.*, 1895, i, 120).—The formula, $C_{13}H_{19}NO_3$, is now assigned to pellotine, and its *mercurochloride* has been prepared. Its third oxygen atom must exist in the form of hydroxyl, for it yields an oily *monobenzoyl* derivative, the *platinochloride* and *aurochloride* of which were prepared. When boiled with methylic iodide and methyl-alcoholic potash, the alkaloid yields *methylpellotine methiodide*, $C_{14}H_{21}NO_3, MeI$, melting at 225° ; from this, the *chloride* and *platinochloride* were prepared; the quaternary ammonium base itself forms hygroscopic crystals which melt at 185° . No well defined products were obtained by heating the alkaloid with hydrochloric acid; in one experiment, the compound $C_{11}H_{12}N(OH)_2 \cdot OMe$ —pellotine with one of its two methoxyl groups replaced by hydroxyl—was obtained, and characterised by means of its yellow *picrate*, which melts at 93° . Of the products obtained by distilling the alkaloid with soda lime or zinc dust, only trimethylamine could be identified; of the products of its oxidation, only oxalic acid.

Alkaloids of *Anhalonium Lewinii*, Hennings (*Lophophora Lewinii*, Rushy).—The dried "discs" (*Scheiben*) of this cactus are used by the Indians of N. Mexico for the preparation of an intoxicant, and are brought into commerce under the name of "Muscale buttons" (from Spanish *Mezcál*, a kind of brandy made from various species of *Agave*). They were extracted with 70 per cent. alcohol, and the residue obtained by evaporating this extract was extracted with ether and then with chloroform. The chloroform dissolved an alkaloid which was named *mezcaline*, whilst the ether dissolved several alkaloids, and by crystallising their sulphates, the sulphate of one, *anhalonidine*, was obtained mixed with some mezcaline sulphate. The

mother liquor was treated with barium chloride, and the hydrochloride of *anhalonine* (Lewin, this vol., i, 194) then obtained from it. From the final mother liquor, the mercurochloride of another alkaloid, *lophophorine*, was obtained and eventually converted into the crystallised *hydrochloride*.

Mezcaline, $C_{11}H_{17}NO_3$, melts at 151° ; it contains three methoxyl groups. The *sulphate* has the composition $(C_{11}H_{17}NO_3)_2 \cdot H_2SO_4 + 2H_2O$; the yellow *platinochloride* is anhydrous.

Anhalonidine, $C_{12}H_{15}NO_3$, melts at 160° , and contains two methoxyl groups; the *hydrochloride* is laevorotatory in solution; the yellowish-red *platinochloride* is anhydrous.

Anhalonine, $C_{12}H_{15}NO_3$, melts at 85.5° (Lewin, 77.5°); it contains one methoxyl group.

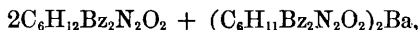
Lophophorine, $C_{13}H_{17}NO_3$, was not obtained crystallised; the yellow *platinochloride* is anhydrous.

All give the same colour reactions, identical with those of pellotine. The following percentages of the pure alkaloids were obtained from the drug: mezcaline, 6.3; anhalonidine (with a little mezcaline), 5.3; anhalonine, 3.0; lophophorine, 0.5.

C. F. B.

Pectase. By GARRIEL BERTRAND and ALFRED MALLEVRE (*Compt. rend.*, 121, 726—728).—See this vol., ii, 267.

The Separation of Lysine. By EDMUND DRECHSEL (*Ber.*, 1895, 28, 3189—3190).—Lysine may be isolated from the products of the decomposition of casein by hydrochloric acid, by converting it first into the dibenzoyl compound, lysuric acid. This is then purified by the recrystallisation of its *acid barium salt*,



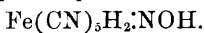
from which the pure lysine can readily be liberated.

A. H.

Organic Chemistry.

Sodium Nitrosoferrocyanide. By KARL A. HOFMANN (*Zeit. anorg. Chem.*, 1896, **11**, 278—287).—The salt, $\text{FeC}_5\text{N}_6\text{O}_2\text{Na}_4\text{H}_{10}\text{H}_2\text{O}$, is obtained by treating an aqueous solution of sodium nitrosoferrocyanide with sodium hydroxide. On adding alcohol to the reddish-yellow solution thus obtained, a yellow syrup is precipitated; it is dissolved in water and again precipitated with alcohol, and then allowed to crystallise in a vacuum over sulphuric acid. Care must be taken to exclude carbonic anhydride, and to maintain the temperature below 15° , for in the presence of carbonic anhydride, sodium nitrosoferrocyanide is re-formed, and at temperatures above 15° decomposition takes place with formation of sodium ferrocyanide, ferric hydroxide, and sodium nitrite. It crystallises in beautiful, yellowish-red, monosymmetric tablets very similar to those of potassium ferricyanide; $\beta = 98\text{--}100^\circ$. It is very easily soluble in water, gives a dark red coloration with ammonium sulphide, and when dried at 110° , yields a yellow powder which is completely soluble in water. The silver salt, $\text{FeC}_5\text{N}_6\text{O}_2\text{Ag}_4\text{H}_2\text{H}_2\text{O}$, is obtained by adding a solution of the sodium salt to a solution of silver nitrate containing ammonium nitrate. It loses its water of crystallisation at 90° .

Methylic nitrosoferrocyanide, $\text{Fe}(\text{CN})_5\text{NOMeH}_2\cdot 2\text{H}_2\text{O}$, is obtained by treating an ice-cold mixture of sodium nitrosoferrocyanide and methylic alcohol with hydrogen chloride, and concentrating the solution in a vacuum over potassium hydroxide and sulphuric acid. It crystallises in red nodules, is easily soluble in water and dilute sodium hydroxide with a reddish-yellow coloration, and gives a characteristic bluish-violet coloration with ammonium sulphide. The *ethylic compound*, obtained in a similar way, crystallises in small, lustrous, bright red plates with $3\text{H}_2\text{O}$, and gives the nitrosoferrocyanide reactions with alkali carbonates and ammonium sulphide. The *propylic compound*, with $3\text{H}_2\text{O}$, crystallises in bright red aggregates, which quickly turn green on exposure to air. From the formation of the above compounds, the author concludes that the nitrosoferrocyanide contains an oximido-group as expressed in the formula



E. C. R.

Composition of the Ohio and Canadian Sulphur Petroleums. By CHARLES F. MABERY (*Amer. Chem. J.*, 1895, **17**, 713—748).—The constituents were separated by distillation in an apparatus somewhat resembling that used in Warren's classical research, but the fractionation was effected under reduced pressure, the latter being regulated by means of an adjustable artificial leak. Ohio petroleum is intermediate in properties between Caucasian and Pennsylvanian oils, and contains the following paraffinoid hydrocarbons: Two butanes (b. p. = 0° and $7\text{--}9^\circ$), pentane and isopentane, hexanes, and heptanes, together

with octane and nonane. These form less than one-tenth of the oil, and correspond with those present in Pennsylvanian oils, of which they form about one-fifth (see next abstract). A. L.

Composition of the Ohio and Canadian Sulphur Petroleums.

By CHARLES F. MABERY (*Amer. Chem. J.*, 1896, **18**, 43—79; compare Abstr., 1894, i, 266, and preceding abstract).—The principal features of the Ohio sulphur petroleum are: (1) The crude oil is heavier than the Pennsylvanian, and lighter than the Russian oil. In the quantities of the higher distillates, and in its general properties it more nearly resembles the latter than the former. (2) It differs from other petroleums in the large amounts of sulphur compounds, which affect its general properties. (3) It resembles the Pennsylvania oil in containing, below 150° , members of the series C_nH_{2n+2} , although in much smaller quantities. The presence of the two isomeric series, C_nH_{2n+2} , in the Ohio oil confirm the observations of Warren on the Pennsylvania petroleum. (4) The aromatic hydrocarbons are present in minute quantities, apparently much smaller than in other petroleums. Benzene, toluene, and meta- and para-xylene have been identified. The hexahydro-series, C_nH_{2n} , is represented by hexahydroisoxylene, and very probably by higher members. Hexahydrobenzene and hexahydrotoluene are not present. (5) By the formation of characteristic nitro-products, and from the results of bromine absorption, the presence in the crude oil of unsaturated hydrocarbons, C_nH_{2n} , seems to be indicated.

The characteristic qualities of the Canadian petroleums are summarised as follows: (1) In its high specific gravity and in the proportions which distil at different temperatures, Canadian petroleum approaches the Russian oil more nearly than it approaches the Ohio petroleum, but the specific gravity of the distillates is lower than that of the Russian distillates. As indicated by its lower specific gravity, Oil Springs oil is essentially different from the Petrolia oil. This is especially evident in the lower percentage of sulphur, the larger quantities of the distillates, the higher specific gravity of these distillates, and the higher bromine absorption. (2) Petrolia oil is composed principally, below 150° , of members of the series C_nH_{2n+2} , although in much smaller quantities even than in Ohio oil (*sic*). Another series is present capable of forming nitro-products resembling the nitro-compounds of the series C_nH_{2n+2} , or the unsaturated hydrocarbons $C_{2n}H_n$ (*sic*). (3) Benzene, toluene, and para- and meta-xylene are present in minute proportions. The hexahydro-series is represented by hexahydroisoxylene, and probably by higher members. (4) The presence of hydrocarbons capable of forming additive products is indicated by the behaviour of the distillates towards bromine, as well as the formation of unsaturated hydrocarbons in the distillates above 200° or 250° , due to cracking. (5) As in Ohio oil, the sulphur compounds have a tendency to collect in the higher fractions.

The paper concludes with some remarks on the origin of petroleum, and it is shown that the limestone petroleums in general contain a higher percentage (up to 0.35 per cent.) of nitrogen than other petroleums do. A. G. B.

Combustion of Acetylene. By HENRI L. LE CHATELIER (*Compt. rend.*, 1895, **121**, 1144—1147).—The combustion of acetylene was investigated by the methods previously employed by the author and Mallard with other gases. Mixtures of acetylene and air containing less than 7.74 per cent. of the former burn completely to carbonic anhydride and water, with a yellowish flame of low illuminating power. With proportions of acetylene between 7.74 and 17.37 per cent., the flame is pale blue with a feeble yellowish aureole, and hydrogen and carbonic oxide are amongst the products of combustion, the relative proportions of these gases being represented by the same formula of equilibrium as in the case of other combustible gases. With more than 17.37 per cent. of acetylene, the reactions are incomplete, and free carbon and unburnt acetylene are present in the gases from the flame as well as hydrogen and carbonic oxide, the flame being red and smoky. The lower and upper limits of combustibility are, with oxygen, 2.8 and 93 per cent. of acetylene respectively, and with air 2.8 and 65 per cent. In a tube 40 mm. in diameter, the velocity of propagation of the flame is 0.1 metre per second with 2.9 per cent. of acetylene, but increases rapidly with the proportion of acetylene until the latter is 8 per cent., when the velocity is 5 metres per second, and afterwards it increases slowly to a maximum of 6 metres per second with 9 to 10 per cent. of acetylene, and beyond this limit it decreases rapidly. The temperature of ignition is only 480°, and hence explosive mixtures of acetylene can be ignited in glass tubes heated with a spirit lamp. The calculated temperature of combustion with 7.74 per cent. of acetylene is 2420°, with 12.2 per cent. 2260°, and with 17.37 per cent. 2100°. When burnt with its own volume of oxygen, the temperature of the flame should be 4000°.

C. H. B.

Homolinalol. By FERDINAND TIEMANN and R. SCHMIDT (*Ber.*, 1896, **29**, 691—695; compare *Abstr.*, 1895, i, 646).—*Homolinalol*,



is obtained by slowly adding a mixture of allylic iodide and methyl-heptenone to granulated zinc in a flask surrounded by a freezing mixture; after remaining at low temperatures during three days, the product is distilled in an atmosphere of steam, homolinalol being separated from the distillate by converting it into the *acetate*, a liquid which boils at 111—117° under a pressure of 15 mm. Homolinalol boils at 102—104° under a pressure of 14 mm., and has an odour which suggests linalol; the sp. gr. = 0.8618 at 20°, and the refractive index $n_D = 1.46534$ at the same temperature, whence the molecular refraction $M = 53.92$. When homolinalol is rapidly heated with camphoric or succinic anhydride, it yields the *hydrocarbon* $\text{C}_{11}\text{H}_{18}$, which boils at 182—185°, has the sp. gr. 0.8415 at 16°, and the refractive index $n_D = 1.47292$, whence the molecular refraction $M = 50.00$. Agitation with 10 per cent. sulphuric acid converts homolinalol into a *compound* which boils at 135—136° under a pressure of 11 mm. Oxidation with potassium permanganate followed by chromic anhydride and sulphuric acid gives rise to

acetone and a small quantity of levulinic acid, along with an acid which is probably methylhydroxyadipic acid,



M. O. F.

Compounds of Sugars with Ethylene Mercaptan, Trimethylene Mercaptan, and Benzyl Mercaptan. By WILLIAM T. LAWRENCE (*Ber.*, 1896, **29**, 547—552; compare *Abstr.*, 1894, i, 269).—*Glucose-ethylenemercaptan*, $\text{C}_6\text{H}_{12}\text{O}_5 \cdot \text{S}_2\text{C}_2\text{H}_4$, is obtained by agitating ethylene mercaptan with a solution of glucose in hydrochloric acid (sp. gr. 1.19); it has a bitter taste, and crystallises from alcohol in colourless, slender needles melting at 143° (uncorr.). Three parts of boiling water dissolve the mercaptan, which is soluble in 12 parts of water at common temperatures, separating from a 10 per cent. solution in pyramids; the specific rotatory power $[\alpha]_D = -10.81^\circ$ in aqueous solution at 20° . The mercaptan is indifferent towards dilute acids, but is readily decomposed by bromine, which gives rise to diethylenic tetrasulphide and glucose.

Mannose-ethylenemercaptan melts at 153 — 154° (uncorr.), and has the specific rotatory power $[\alpha]_D = +12.88^\circ$ at 20° . *Galactose-ethylenemercaptan* melts at 149° (uncorr.), and does not crystallise readily; *arabinose-ethylenemercaptan* melts at 154° (uncorr.), and dissolves in 8 parts of water. *Rhamnose-ethylenemercaptan* crystallises from alcohol in slender, colourless needles, and melts at 169° (uncorr.); *xylose-ethylenemercaptan* resembles the derivatives of glucose and rhamnose.

Glucose-trimethylenemercaptan, $\text{C}_6\text{H}_{12}\text{O}_5 \cdot \text{S}_2\text{C}_3\text{H}_6$, crystallises from alcohol in slender needles, which taste bitter and melt at 130° ; it dissolves in $1\frac{1}{2}$ parts of boiling water and 15 parts of boiling alcohol, being soluble in 9 parts of water at the ordinary temperature. *Arabinose-trimethylenemercaptan* crystallises in long needles, has a bitter taste, and melts at 150° (uncorr.); *galactose-trimethylenemercaptan* and *xylose-trimethylenemercaptan* are colourless syrups.

Glucose-benzylmercaptan, $\text{C}_6\text{H}_{12}\text{O}_5(\text{SCH}_2\text{Ph})_2$, crystallises from 50 per cent. alcohol in slender, white needles, and melts at 133° (uncorr.); it has a bitter taste, and dissolves in 8 parts of boiling alcohol, but requires 50 parts of boiling water. *Galactose-benzylmercaptan* melts at 130° (uncorr.), and dissolves in 6 parts of hot alcohol; *rhamnose-benzylmercaptan* crystallises in plates, and melts at 125° . *Arabinose-benzylmercaptan* crystallises from 50 per cent. alcohol in very long needles, and melts at 144° ; *xylose-benzylmercaptan* is a syrup.

M. O. F.

Crystallised *d*-Mannose. By W. ALBERDA VAN EKENSTEIN (*Rec. Trav. Chim.*, 1895, **14**, 329).—The author has obtained *d*-mannose crystallised in the form of prisms, which are only slightly hygroscopic; its aqueous solution shows multirotation, at first being levogyrate, but afterwards dextrogyrate.

J. J. S.

Crystallised Anhydrous Rhamnose. By EMIL FISCHER (*Ber.*, 1896, **29**, 324—325).—Tanret (*Compt. rend.*, 1896, **122**, 86) has overlooked the fact that the author has already prepared this substance by heating ordinary rhamnose on the water bath and crystallising

the product from acetone (Abstr., 1895, i, 440). In 10 per cent. aqueous solution at 20°, the specific rotation is $[\alpha]_D = +31.5$ one minute after the substance has been dissolved; after half an hour, it is only +18°, and it sinks eventually to the value generally ascribed to rhamnose.

C. F. B.

Volemitol, a new Saccharine Matter. By EMILE E. BOURQUELOT (*J. Pharm.*, 1895, [6], 2, 385—390).—To prepare volemitol (Abstr., 1895, i, 639), 500 grams of the dried fungus *Lacterius volemus* is digested for 20 minutes, on a water bath, with two litres of 85° alcohol, or, if the fresh fungus is used, 95° alcohol is employed; the hot alcohol is decanted, the digestion repeated with 1.5 litre of fresh alcohol and the residue pressed. The combined liquors are filtered when cold, the alcohol distilled off, and the residue concentrated to a syrup which is extracted with 95° alcohol; from this solution, volemitol is very slowly deposited. It is purified by dissolving it in boiling 80° alcohol, using 8 parts of solvent to 1 of volemitol, filtering, warming, allowing to crystallise, drying with the air pump, and washing first with 95° alcohol, then with ether, and finally drying at 60°. Volemitol forms little spherical accumulations of minute, fine, white, soluble needles, the melting point, specific rotation, &c., for a pure sample are given in the abstract referred to. It contains no water of crystallisation, and decomposes when heated above 200°, evolving water and an odour of caramel. It is faintly sweet, is very soluble in water, but only slightly so in alcohol; the solubility, in the latter case, however, being increased by the presence of certain organic compounds. It does not reduce Fehling's solution even after treatment with boiling dilute sulphuric acid, nor is it fermented by yeast. It prevents the precipitation of copper oxide by alcohol, but produces a blue precipitate in ammoniacal copper sulphate. The author has not obtained any nitro-derivative, and when digested at the boiling point for 1½ hour with anhydrous sodium acetate, and acetic anhydride, it yields a crystalline compound having the properties of mannitol hexacetate, but, unlike mannitol, when digested only 20 minutes, no crystalline product is obtained. With acetaldehyde and benzaldehyde, it forms acetals, which crystallise in silky needles. The ethylic acetal is very soluble in boiling 75° alcohol; it melts at 190° and is lævoptatory.

D. A. L.

Dextrins obtained by the Hydrolysis of Starch. By K. BÜLOW (*Pflüger's Archiv*, 1895, 62, 131—155).—The author has obtained amylopectrin by adding pure potato starch in small quantities to an equal weight of potash dissolved in water. The mixture is warmed on the water bath, and finally, for about 10 minutes, over a free flame; the amylopectrin may then be precipitated by alcohol, and if the directions are carefully followed, it is obtained in the form of a colourless powder which can easily be filtered off. It is best purified by repeated solution in hot water and precipitation by absolute alcohol, when it is obtained in the form of a white solid which, when quite free from alcohol, is not affected by exposure to air. It is only sparingly soluble in water, even when hot, and yields an opalescent

solution, from which after a time, a portion of the dextrin separates. With iodine solution, it gives a blue coloration, and does not reduce Fehling's solution, even on boiling with it for some time.

The author has also obtained amylo-dextrin from starch by digesting it at 60° for 10–15 minutes with a chloroform solution of diastase. If the digestion is continued for too long a time, erythro-dextrin is obtained together with amylo-dextrin. Attempts to separate the two dextrans by means of fractional precipitation with baryta solution proved useless, the method of dialysis is also too slow for the separation of the two, but may be used for the detection of erythro-dextrin in a sample of amylo-dextrin. Both amylo-dextrans were partially precipitated by barium hydroxide solution and the precipitate analysed. The precipitate obtained from the amylo-dextrin from potato starch had the composition: Dextrin: $\text{Ba}(\text{OH})_2 = 100 : 13.25$, which agrees well with the formula $(\text{C}_6\text{H}_{10}\text{O}_5)_8, \text{Ba}(\text{OH})_2$.

Amylo-dextrin obtained from starch by means of dilute sulphuric acid has the same properties as that obtained by means of potash or diastase; but all three differ materially from the amylo-dextrin described by Lintner and Düll (Abstr., 1894, i, 5), especially as regards their solubility in hot water. The author considers his compound to be pure amylo-dextrin, and thinks that the substance described by Lintner and Düll is merely a mixture of his amylo-dextrin with erythro-dextrin. A half per cent. solution of amylo-dextrin in water is immediately gelatinised when treated with a 20 per cent. sodium hydroxide solution. The gelatinised mass becomes liquid on warming, but again solidifies on cooling, and is readily soluble in cold water. Potassium hydroxide does not act in the same way.

Erythro-dextrin was prepared by treating starch paste with diastase at 60 – 70° until it gave a clear red coloration with iodine. After destroying the diastase by boiling and evaporating, the erythro-dextrin was precipitated by means of alcohol, and freed from achroo-dextrin by treatment with excess of barium hydroxide, whereby the barium compound of erythro-dextrin was thrown down while the achroo-dextrin remained in solution. The erythro-dextrin was also prepared by slightly modified methods, but in all cases it forms a snow-white powder, which is not altered when exposed to air. It is readily soluble in water, yields a brownish-red coloration with iodine solution, and does not reduce alkaline copper sulphate solution at the ordinary temperature. The solution was precipitated with an insufficient quantity of barium hydroxide, when a compound was obtained, probably having the formula $(\text{C}_6\text{H}_{10}\text{O}_5)_5, \text{Ba}(\text{OH})_2$, or $(\text{C}_6\text{H}_{10}\text{O}_5)_6, \text{Ba}(\text{OH})_2$. The rotatory power in all cases is about $[\alpha]_D = 190$, even when the erythro-dextrin is mixed with achroo-dextrin.

Achroo-dextrin was obtained by treating starch paste with diastase at 60 – 70° until it remained colourless when treated with iodine. After boiling to destroy the diastase, it was precipitated by 96 per cent. alcohol. It forms a snow-white powder readily soluble in water and is not precipitated from its aqueous solution by barium hydroxide, but can be precipitated in this way from an alcoholic solution, yielding a compound $(\text{C}_6\text{H}_{10}\text{O}_5)_4, \text{Ba}(\text{OH})_2$. Its specific rotatory power is $[\alpha]_D = +179$ – 184° , and it readily reduces Fehling's solution.

Attempts to further purify the achroodextrin (1) by treatment with phenylhydrazine, (2) by partial oxidation with alkaline copper sulphate solution, (3) by Landwehr's iron precipitation method proved fruitless, but the author thinks that it is quite possible either by fractional precipitation with barium hydroxide in a 10 per cent. alcoholic solution, or by dialysis, or by a combination of both methods, to prepare an achroodextrin with constant properties and finally to make a molecular weight determination.

J. J. S.

Reduction Products of Methylbutylnitramine. By ANTOINE P. N. FRANCHIMONT and H. VAN ERP (*Rec. Trav. Chim.*, 1895, **14**, 317—326; compare *Abstr.*, 1885, 963).—A mixture of methylbutylamine and methylbutylhydrazine was obtained by reducing methylbutylnitramine with zinc dust and acetic acid. The two are best separated by treatment with ethylic oxalate, since the hydrazine yields oxalmethylbutylhydrazide and the amine methylbutyloxamic acid.

Oxalmethylbutylhydrazide, $C_2O_2(NH \cdot NMe \cdot C_4H_9)_2$, is a colourless, crystalline substance; it melts at 156° , and is moderately soluble in boiling alcohol. When boiled with aqueous potash and then distilled, it yields *methylbutylhydrazine*, which boils at $50.5\text{--}51^\circ$ under 38 mm. pressure; it is a colourless liquid, of sp. gr. = 0.8092 at 15° , and is miscible in all proportions with water, alcohol, and ether. Its *hydrochloride* is extremely hygroscopic, and therefore difficult to prepare, and its *platinohydrochloride* does not crystallise readily. When an ethereal solution of the hydrazine is treated with yellow mercuric oxide, it yields *methylbutyltetrazone*; this distils at $119\text{--}120^\circ$ under 18 mm. pressure, and is a colourless liquid of sp. gr. = 0.8798 at 15° . It is only sparingly soluble in water, has an alkaline reaction, and does not reduce Fehling's solution. The mother liquors from the oxalmethylbutylhydrazide were treated with nitrous acid, in order to convert any of the hydrazine into methylbutylamine, and, after dilution with water, were distilled.

Methylbutylamine is a colourless liquid with a slight ammoniacal odour, and is readily soluble in water, alcohol, and ether. It has a sp. gr. = 0.7375 at 15° , boils at $90.5\text{--}91.5^\circ$ under 764 mm. pressure, and does not reduce Fehling's solution. The authors contradict Zublin's statement (*Abstr.*, 1878, 284) that normal butylamine reduces Fehling's solution. The *hydrochloride*, $NHMe \cdot C_4H_9 \cdot HCl$, crystallises in small plates, melts at $170\text{--}171^\circ$, is extremely hygroscopic, and is soluble in water, alcohol, and chloroform. The *platinohydrochloride* is readily soluble in water, sparingly in alcohol, and melts at 203° , at the same time undergoing decomposition.

Methylbutylnitrosamine is a yellow liquid, only slightly soluble in water, but miscible with alcohol and ether; its sp. gr. = 0.936 at 15° , and it boils at $84\text{--}85^\circ$ under 15 mm. pressure, and at $199\text{--}201^\circ$ under 767 mm. pressure.

J. J. S.

Action of Fused Potash on Methylnitramine and Dimethylnitramine. By H. VAN ERP (*Rec. Trav. Chim.*, 1894, **14**, 327—328,

and *Ber.*, 1896, **29**, 474—476).—When dimethylnitramine is fused with potash, it yields potassium nitrite and ethylamine, which was recognised by conversion into dinitromonomethylaniline. Methyl-nitramine, when treated in a similar manner, yields a mixture of hydrogen and ammonia, together with formic and nitrous acids. These results are at variance with the statements of Thiele and Lachmann (*Abstr.*, 1895, i, 587), according to whom the nitramines yield nitric acid and methylamine and dimethylamine respectively.

A. H.

Dimethylglyoxime. By ENRICO RIMINI (*Gazzetta*, 1895, **25**, ii, 266—268).—The glyoxime peroxides, $\begin{array}{c} \text{CR} - \text{CR}' \\ || \quad || \\ \text{NO} - \text{ON} \end{array}$, on reduction with tin and hydrochloric acid, yield furfurazinic derivatives, whilst, on reduction with zinc dust and acetic acid, they give syn-dioximes. Dimethylglyoxime peroxide, when treated with zinc dust and acetic acid, yields the dimethylglyoxime obtained by Fittig (*Abstr.*, 1889, 490) by the action of hydroxylamine on diacetyl. This glyoxime is therefore a syn-glyoxime, as is also indicated by the readiness with which it yields dimethylazoxazole (Wolff, *Abstr.*, 1895, i, 182).

W. J. P.

Action of Hydroxylamine Hydrochloride on Glyoxal. By ARTURO MIOLATI (*Gazzetta*, 1895, **25**, ii, 213—217).—On preparing glyoxime by the action of hydroxylamine on glyoxal in acid solution, the crude product contains a certain proportion of an explosive *substance*, which is obtained pure by evaporating a concentrated solution of hydroxylamine hydrochloride and glyoxal until crystallisation begins, and then neutralising exactly with sodium carbonate; the crystalline precipitate is extracted with ether to remove glyoxime, and crystallised from boiling water, when colourless needles are obtained of the composition $\text{C}_4\text{H}_5\text{N}_3\text{O}_3$, melting and decomposing at 176° . When heated on a spatula, it explodes like gun-cotton, leaving no residue, and is sparingly soluble in cold water, alcohol, or ether; it is readily soluble in acids, alkalis, or alkali carbonates, but is precipitated unaltered on carefully neutralising the solution. It is slowly decomposed when boiled with acetic anhydride or chloride. It yields a *benzoyl* derivative, which was not analysed; its *hydrochloride*, $\text{C}_4\text{H}_5\text{N}_3\text{O}_3 \cdot \text{HCl}$, crystallises in needles melting at the same temperature as the base, and the *platinochloride* is very soluble in water and explodes on heating. The base probably has the constitution $\text{CH} \leq \begin{array}{c} \text{C}(\text{NOH}) \\ \text{N} \text{---} \text{O} \end{array} > \text{CH} \cdot \text{CH} \cdot \text{NOH}$, and is not formed by the action of hydroxylamine on glyoxal in neutral or alkaline solutions, therefore glyoxime should be capable of being prepared under such conditions.

W. J. P.

Action of Halogens on Formaldehyde. By ANDRÉ BROCHET (*Compt. rend.*, 1895, **121**, 1156—1159).—Dry chlorine has no action on trioxymethylene in diffused daylight at the ordinary temperature, but, on gently heating, hydrogen chloride and carbonic oxide are

given off. In direct sunlight, carbonic chloride is also formed, but it is a secondary product, resulting from the action of excess of chlorine on carbonic oxide, and the quantity produced is greater the more rapid the current of chlorine.

A mixture of 1 gram of trioxymethylene and 1 c.c. of bromine at the ordinary temperature forms a dry powder, which, when allowed to remain at the ordinary temperature in the dark or in diffused daylight, gradually liquefies and acquires a blood-red colour. In sunlight, these changes are much more rapid, but in both cases a gas is liberated which contains a high proportion of carbonic oxide. At 100°, the solid mixture liquefies at once, but gas is only very slowly liberated, and it contains a lower proportion of carbonic oxide with some carbonic anhydride. In all these cases, some carbonic bromide is formed, probably as a result of the action of bromine on the carbonic oxide.

In all cases, the action of chlorine or bromine on formaldehyde produces carbonic oxide, and this result explains the occurrence of carbonic oxide in the products of the action of halogens on methylic alcohol (Abstr., 1895, i, 637).

When methylic alcohol is burnt with a limited quantity of oxygen, from 5 to 10 per cent. is converted into formaldehyde, and from 3 to 5 per cent. into carbonic oxide, whilst the rest is completely burnt to carbonic anhydride and water.

C. H. B.

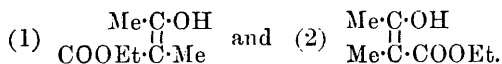
Tetrinic [Tetric] acid. By PAUL C. FREER [and, in part, E. R. MILLER] (*Amer. Chem. J.*, 1895, 17, 779—726).—The author's results are not in accordance with those of Nef (see Abstr., 1892, 140). The product of bromination of ethylic methylacetoacetate or its sodium derivative is not a single substance, and contains unaltered ethylic methylacetoacetate, and ethylic α - and γ -monobromo- and dibromomethylacetoacetates. It may be partially resolved by distillation, the different fractions yielding, under the same conditions, different proportions of tetric acid. On oxidising the mixture by cold alkaline permanganate, a small quantity of oxalic acid is obtained, together with chloroacetic acid and much acetic acid, the first two obviously being produced by the oxidation of the γ -bromo-derivative, and the latter from the β -derivative. The total amount of γ -derivative present in a specimen prepared by the author is estimated at 6 per cent., a specimen prepared from Kahlbaum's ethylic methylacetoacetate containing much less.

The isomeric ethylic bromomethylacetoacetates may be partially separated by means of alkalis, in which the α -derivative is insoluble; after treatment in this manner, the α -derivative yielded no tetric acid, the presence of hydrobromic acid being necessary to effect an initial change to the γ -derivative, which alone affords tetric acid when distilled or heated.

Ethylic bromomethylacetoacetate, on being heated at 100° for some time, yields 87.4 per cent. of the theoretical quantity of tetric acid, and a small quantity of hydrogen bromide may be detected in the liberated gases.

As different samples of apparently pure ethylic methylacetoacetate

differ in behaviour when brominated, it is possible that there exist together the geometric isomerides



(1) would give a γ -derivative which would readily evolve ethylic bromide and yield tetric acid; (2) would merely change gradually by molecular re-arrangement.

With E. R. MILLER.—Contrary to Demarçay's account, silver tetratate is fairly soluble in water, and is used for the preparation of ethylic tetratate, the vapour density of which, at 174° , agrees with the formula $\text{C}_5\text{H}_5\text{O}_3\text{Et}$. The *benzoyl* derivative of tetric acid, obtained by the action of benzoic chloride on sodium tetratate, separates from acetone in long, lustrous needles, melting at 128° , and is partially decomposed by boiling alcohol, ethylic benzoate being formed. Its molecular weight in boiling benzene is normal. *Tetric chloride*, contrary to the statements of Wolff (this vol., i, 887), is capable of existence, and has a normal vapour density; it dissolves slowly in alkalis, thus evincing its lactonic character. As in the case of ethylic tetratate, a liquid and a solid modification have been obtained. A. L.

Action of Inorganic acidic Metallic Oxides on Organic acids.

By ARTHUR ROSENHEIM [and, in part, LUDWIG COHN] (*Zeit. anorg. Chem.*, 1896, **II**, 175—222; see also Abstr., 1893, i, 626).—I. *Aluminium Oxalates* [with LUDWIG COHN].—When a solution of oxalic acid is saturated with an excess of alumina and the filtrate evaporated on the water bath, a clear, pale yellow syrup is obtained, which contains the compound $\text{Al}_2\text{O}_3, 3\text{C}_2\text{O}_3$. It cannot be obtained in crystals, gives no precipitate when treated with alcohol or ether, solidifies to a homogeneous, white mass when cooled to -15° , and melts again at -5° . It gives no reaction with vanadic acid, showing that it contains no free oxalic acid, gives an acid reaction towards indicators, and when boiled with ammonia is decomposed, with formation of a complex ammonium salt and precipitation of about half the aluminium as hydroxide. With chlorides of the metals, it forms well-characterised compounds containing alumina. The *barium salt*, $\text{Al}_2\text{Ba}_3(\text{C}_2\text{O}_4)_6 + 6\text{H}_2\text{O}$, crystallises in silky, lustrous needles, and is partially decomposed on recrystallisation.

A *double salt*, of the composition $\text{Al}_2\text{K}_6(\text{C}_2\text{O}_4)_6 + 5\text{H}_2\text{O}$, is obtained by treating a boiling solution of acid potassium oxalate with excess of alumina; it crystallises in large, colourless, prismatic needles, gives most of the reactions for aluminium, except that only part of the aluminium is precipitated by boiling with ammonia. With calcium chloride, it yields a compound containing aluminium, and calcium oxalate is not precipitated. The corresponding sodium and ammonium salts, with $9\frac{1}{2}$ and $5\frac{1}{2}$ H_2O respectively, are obtained in a similar manner. The salts are likewise obtained by treating the above aluminium oxalate with the corresponding chlorides. They give up their water of crystallisation when heated at 80 — 90° , and do not reduce vanadic acid.

A salt, of the composition $2\frac{1}{2}\text{K}_2\text{O}, \text{Al}_2\text{O}_3, 5\text{C}_2\text{O}_3, 5\text{H}_2\text{O}$, is obtained by saturating a boiling solution of acid potassium oxalate with excess of alumina, concentrating the solution in presence of excess of alumina over a bare flame, and, after rapid filtration, evaporating it to crystallisation; it forms rhombic scales, and decomposes on recrystallisation. The *sodium salt* with $8\text{H}_2\text{O}$ separates in nodules or rhombic crystals, and effloresces rapidly on exposure to air. The *ammonium salt* was not obtained, as the solution on concentration gives off ammonia and the salt $3(\text{NH}_4)_2\text{O}, \text{Al}_2\text{O}_3, 6\text{C}_2\text{O}_3, 5\frac{1}{2}\text{H}_2\text{O}$, then separates. These salts contain one-OH group, as shown by the fact that the last $\frac{1}{2}$ mol. of water is only given off at 130° . They dissolve vanadic acid with a yellow coloration, have a neutral reaction, and give crystalline precipitates of double aluminium oxalates when treated with chlorides of the alkaline earths. When dissolved in water, they decompose according to the equation $3\text{OH}\cdot\text{Al}_2(\text{OOC}\cdot\text{COOR})_3 = 5\text{Al}(\text{OOC}\cdot\text{COOR})_3 + \text{Al}(\text{OH})_3$, and can therefore only be obtained in the presence of an excess of alumina.

The salt $2\text{K}_2\text{O}, \text{Al}_2\text{O}_3, 4\text{C}_2\text{O}_3, 3\text{H}_2\text{O}$ is obtained by slowly adding potassium hydroxide (1 mol.) to a solution of acid potassium oxalate (5 mols.) saturated with alumina. It crystallises in rhombic scales, and is easily soluble in cold and warm water, but these solutions at once decompose with separation of alumina. The *sodium salt* with 6 and $7\text{H}_2\text{O}$ crystallises in small plates. The *ammonium salt* crystallises with $2\text{H}_2\text{O}$. These salts give similar reactions to the preceding, and contain $1\text{H}_2\text{O}$ more intimately combined. Salts more basic than the above cannot be obtained. When a solution containing the constituents in the proportion $2\frac{1}{2}\text{K}_2\text{O}, \text{Al}_2\text{O}_3, 5\text{C}_2\text{O}_3$ is treated with 2 or 3 mols. of potassium hydroxide, alumina is precipitated, and the preceding salts, together with normal oxalates, are obtained.

The salt $\text{K}_2\text{O}, \text{Al}_2\text{O}_3, 4\text{C}_2\text{O}_3, 7\frac{1}{2}\text{H}_2\text{O}$ is obtained by adding to a filtered solution of oxalic acid (3 mols.), saturated with alumina, a concentrated solution of normal potassium oxalate (1 mol.) evaporating to a syrup, and then stirring well with a glass rod. The salt crystallises in microscopic tablets, and can be recrystallised without decomposition. The *sodium* and *ammonium* salts are similar, and crystallise with $10\frac{1}{2}$ and 5 H_2O respectively. These salts give a faintly acid reaction, do not react with vanadic acid, and give crystalline double aluminium oxalates when treated with chlorides of the alkaline earths. Only part of the aluminium is precipitated by boiling with ammonia.

II. *Alkali Chromium Oxalate*.—When a boiling solution of oxalic acid is saturated with an excess of freshly precipitated chromium hydroxide, a deep bluish-red syrup is obtained which will not crystallise, is completely soluble in alcohol and ether, and contains the constituents in the ratio $\text{Cr}_2\text{O}_3, 3\text{C}_2\text{O}_3$. Neither the oxalic acid nor the chromium hydroxide can be detected by the ordinary methods. With chlorides of the alkaline earths, the compound gives beautifully crystalline salts containing chromium. With ammonia, no precipitate is obtained, and by prolonged boiling with excess of caustic alkali, a voluminous green precipitate is obtained. The *barium salt*, $\text{Cr}_2\text{Ba}_3(\text{C}_2\text{O}_4)_6, 8\text{H}_2\text{O}$, crystallises in bright green needles

having a red fluorescence, and has been previously obtained by Werner.

The salts of the composition $3R_2O, Cr_2O_3, 6C_2O_3$, are obtained in a similar way to the preceding aluminium compounds, and are blue to bluish-red. The potassium salt crystallises with $6H_2O$ in monoclinic scales, the sodium salt with $9H_2O$ in tablets, and the ammonium salt with $6H_2O$ in leaflets.

The salts of the composition $2\frac{1}{2}R_2O, Cr_2O_3, 5C_2O_3$ cannot be prepared. A green syrup containing the constituents in the right proportions is obtained in a similar manner to that described for the preparation of the aluminium compounds, but this syrup quickly decomposes with separation of chromium oxide, and then the preceding blue salts crystallise out. In one experiment, by cooling the green syrup to -20° , green needles were obtained, but they decomposed so rapidly that an analysis was not possible.

The salt, $2K_2O, Cr_2O_3, 4C_2O_3, H_2O$, is obtained in a similar manner to the corresponding aluminium salt; it crystallises in deep green, microscopic needles. The sodium salt has also been obtained crystalline. The ammonium salt could not be obtained crystalline, but formed a gummy mass containing chromium oxide.

The salt, $K_2O, Cr_2O_3, 4C_2O_3, 10H_2O$, is obtained in a similar manner to the corresponding aluminium salt; it crystallises in beautiful deep red prisms.

III. *Alkali Ferric Oxalates*.—The author has examined the iron compounds obtained in a similar manner to the preceding. By the action of oxalic acid on freshly prepared ferric hydroxide, a deep yellow syrup is obtained, containing the constituents in the ratio $Fe_2O_3 : 3C_2O_3$. *Alkali iron oxalates* of the series $3 : 1 : 6$ are obtained by saturating solutions of the acid alkali oxalates with ferric hydroxide. The salts of the composition $2\frac{1}{2}R_2O, Fe_2O_3, 5C_2O_3$, like the preceding chromium compounds, cannot be obtained crystalline, although the analysis of the solution indicates their presence. The salts of the series $2 : 1 : 4$ could not be prepared, and attempts to obtain them yielded green salts of the series $3 : 1 : 6$, together with a brownish-red precipitate of variable composition containing all three constituents. The salt $K_2O, Fe_2O_3, 4C_2O_3, 5H_2O$, obtained in a similar manner to the aluminium salt, crystallises in bright brown crystals, and is decomposed when recrystallised, with formation of the green salt ($3 : 1 : 6$) and separation of ferric hydroxide.

The salt, $K_2O, Fe_2O_3, 4MoO_3, 2C_2O_3, 10H_2O$, is obtained in beautiful bright yellow crystals by saturating a solution of the salt $3K_2O, Fe_2O_3, 6C_2O_3, 6H_2O$ with molybdic acid.

IV. Of the five types of compounds described, all the aluminium compounds, four of the chromium compounds, and three of the iron compounds are capable of existence, that is, the number of the complex acids varies with the basicity of the trivalent metal. The normal tribasic salts of the type $M'''(OOC \cdot COOR)_3$ are the most stable, and are easily obtained from the sesquioxides of iron, aluminium, and chromium, and also, though less easily, from the oxides of manganese and cobalt. By the addition of oxalic acid groups to the sesquioxides, acids are formed, which are stronger

and more capable of forming salts according as more hydroxyl groups of the sesquioxide are replaced by oxalic acid groups, and also according to the less basic character of the sesquioxide.

E. C. R.

Derivatives of Tartaric and Parapyruvic acids. By EDUARD MULDER (*Rec. Trav. Chim.*, 1895, **14**, 281—306; compare Abstr., 1893, i, 685, and 1895, i, 449).—The author has continued his investigations on the products respectively soluble and insoluble in acetic acid, which result from the action of ethylic chloride on ethylic disodium tartrate.

On treatment with baryta water, a mixture of two substances was obtained. One of these, the crystalline barium compound, is shown to be barium oxalate, $\text{BaC}_2\text{O}_4 + 2\text{H}_2\text{O}$; it loses $1\frac{1}{2}\text{H}_2\text{O}$ at 120° , and the remaining $\frac{1}{2}\text{H}_2\text{O}$ at 120 — 140° . The other substance, the mamellated compound, when freed from barium oxalate, yields racemic acid, and a second crystalline acid, the constitution of which has not yet been determined. These three acids, oxalic, racemic, and the acid of unknown constitution, are regarded as decomposition products of tartryltartaric acid.

The author recommends slight modifications in the preparation of ethylic tartrates, and also in the manner of treatment of ethylic disodium tartrate with ethylic chloride.

Barium parapyruvate has the composition, $(\text{C}_3\text{H}_3\text{O}_3)_2\text{Ba} + \text{H}_2\text{O}$; parapyruvic acid itself is unstable, and readily loses carbonic anhydride and water.

J. J. S.

Stereoisomeric Dimethyltricarballic acids. By NICOLAI D. ZELINSKY and N. TSCHERNOSWITOFF (*Ber.*, 1896, **29**, 333—339).—Ethylic cyanodimethylcarballylate, $\text{COOEt}\cdot\text{C}(\text{CN})(\text{CHMe}\cdot\text{COOEt})_2$ (compare Barthe, Abstr., 1888, 937, and *Ann. Chim. Phys.*, 1892, [6], **27**, 281), was prepared by the action of ethylic cyanacetate on ethylic α -bromopropionate in the presence of sodium ethoxide, the fraction boiling at 190 — 210° (for the most part at 195 — 197°) being used for the further experiments. When heated with dilute sulphuric acid (1:1), it yields three acids, all of which have the composition, $\text{C}_8\text{H}_{12}\text{O}_6$, that is, $\text{COOH}\cdot\text{CH}(\text{CHMe}\cdot\text{COOH})_2$; one of these is fairly insoluble in water, and melts at 203 — 204° ; by fractional crystallisation of the mother liquor from this acid, the other two, melting respectively at 175 — 176° and 148 — 149° , were obtained. All three, when warmed with acetic chloride, yield crystallised isomeric anhydrides, $\text{C}_8\text{H}_{10}\text{O}_5$, melting respectively at 111 — 113° , 129 — 130° , and 117 — 119° , and these re-unite with water, reforming the original acids. But the acids also yield anhydrides, transparent, and viscid in character, when they are heated alone at 200 — 210° , and these, with water, regenerate the original acids, with the exception of the anhydride of the acid melting at 203 — 204° , which yields the acid melting at 148 — 149° . Further, the second and third acids are both transformed into the first (melting at 203 — 204°) when heated with hydrochloric acid at 190 — 200° . The isomerism of these three acids is, doubtless, of stereochemical nature.

C. F. B.

Preparation of Amides and Acid Chlorides. By ALBERT COLSON (*Compt. rend.*, 1895, **121**, 1155—1156).—When dry hydrogen chloride is passed into a mixture of a nitrile and an acid cooled at about 0°, an amide and an acid chloride are formed, $\text{RCN} + \text{R}'\text{COOH} + 2\text{HCl} = \text{RCO}\cdot\text{NH}_2\cdot\text{HCl} + \text{R}'\text{COCl}$. Acetonitrile and acetic acid yield acetamide and acetic chloride; acetonitrile and propionic acid yield acetamide and propionic chloride; acetic acid and propionitrile yield propionamide and acetic chloride. Formic acid, under similar conditions, decomposes in a different manner. The well-known efficiency of hydrogen chloride in promoting the formation of ethereal salts is probably due to its tendency to convert acids into acid chlorides in presence of any substance which will combine with water.

Acid chlorides are formed still more easily if the acid in the above reaction is replaced by the anhydride. C. H. B.

Method of Decomposition of some Amides and Imides. By WILLIAM ECHSNER DE CONINCK (*Compt. rend.*, 1895, **121**, 893—894).—The author has investigated the behaviour of various amides and imides with a solution of sodium hypochlorite, prepared by precipitating a solution of 50 parts of fresh bleaching powder in 500 parts of water, with a solution of 100 parts of sodium carbonate in 300 parts of water.

Formamide is decomposed slightly at the ordinary temperature, and more rapidly on heating. Acetamide is not decomposed, even when moderately heated. Propionamide begins to decompose in the cold, and the change becomes very rapid on heating; butyramide also decomposes on heating. Oxamide and succinamide behave like propionamide. Glycocine, amidopropionic acid (alanine), and asparagine decompose when gently heated; but hippuric acid is not decomposed unless strongly heated. Succinimide decomposes very rapidly, even at the ordinary temperature. In all cases the gas liberated has the negative properties of nitrogen. C. H. B.

New Salts of Amides. By J. TOPIN (*Ann. Chim. Phys.*, [7], **5**, 99—132).—*Basic acetamide hydrobromide*, $(\text{C}_2\text{H}_5\text{NO})_2\cdot\text{HBr}$, is obtained when a solution of acetamide in equal parts of alcohol and ether is treated with pure, dry, gaseous hydrogen bromide. It is necessary to pass the gas in a slow stream, and to keep the vessel containing the solution of acetamide cool by means of cold water. The hydrobromide crystallises in colourless, odourless, fragile needles, which have an acid taste and reaction. It melts at 139.5°, and shortly afterwards decomposes, is readily soluble in water, sparingly in alcohol, and insoluble in ether, and is decomposed by alkalis.

The author was not able to prepare acetamide hydriodide.

Acetamide platinumchloride, $(\text{C}_2\text{H}_5\text{NO})_2\cdot\text{H}_2\text{PtCl}_6$, obtained from aqueous solutions of acetamide and platinum chloride, is an orange-yellow crystalline powder, which is very sparingly soluble in water, even less so in alcohol, and melts and decomposes at 225°.

Acetamide hydrogen oxalate, $\text{C}_2\text{H}_5\text{NO}\cdot 2\text{C}_2\text{H}_2\text{O}_4$, is best obtained by adding acetamide (1 mol.) in concentrated aqueous solution to oxalic acid (2 mols.), also in aqueous solution; it is also formed when the

two compounds, in molecular proportion, are mixed in aqueous or alcoholic solution. It crystallises in colourless prisms or plates, and melts at 129° .

Another *oxalate*, $C_2H_5NO \cdot C_2H_2O_4$, was obtained by the author on adding the amide (2 mols.) to oxalic acid (1 mol.); it forms small, colourless, brilliant prisms, which are readily soluble in water and in alcohol, and redden blue litmus.

The *acid tartrate*, $C_2H_5NO \cdot C_4H_6O_6$, is best obtained by treating acetamide in alcoholic solution with an excess of tartaric acid. It crystallises in colourless plates, melts at 130.5° , is extremely soluble in water, more sparingly in alcohol, and has an acid reaction. It is decomposed on heating, and also, like all the other salts of amides, on treatment with alkalis.

The *normal tartrate*, $(C_2H_5NO)_2 \cdot C_4H_6O_6$, is obtained when 2 mols. of the amide are taken for each molecule of acid. It forms short, brilliant crystals, with small facets; on heating, it turns brown at 190° , and decomposes at about 225° .

Acetamide picrate, $C_2H_5NO \cdot C_6H_3N_3O_7$, may easily be prepared by the action of picric acid on acetamide in alcoholic solution, or by dissolving the amide in fused picric acid. The salt is moderately soluble in alcohol, somewhat more sparingly in water. When carefully heated, it melts at 117.5° . It crystallises in small prisms, of a brilliant yellow colour.

Normal oxamide tartrate, $(C_2H_4N_2O_2)_2 \cdot C_4H_6O_6$, crystallises in small, orthorhombic plates; it dissolves readily in water, more sparingly in alcohol; it has acid properties, and in aqueous solution is dextro-rotatory, practically to the same extent as the normal acetamide tartrate (compare Wyruboff, Abstr., 1894, ii, 177).

Basic acetanilide hydrobromide, $2C_6H_5NO \cdot HBr$, may be prepared in much the same way as the acetamide hydrobromide. It crystallises in small, colourless needles, which are readily soluble in water and in alcohol, but almost insoluble in ether.

Acetanilide platinumchloride, $(C_6H_5NO)_2 \cdot H_2PtCl_6$, crystallises in orange-yellow needles, which are only very sparingly soluble in water and in alcohol.

Acetanilide picrate, $C_6H_5NO \cdot C_6H_3N_3O_7$, crystallises in yellow prisms. It is but sparingly soluble in water and in alcohol, and decomposes when gently heated.

The crystallographic properties of most of the salts are given in detail. J. J. S.

Synthesis of Complex Amides. By ALBERT COLSON (*Compt. rend.*, 1895, 121, 825—827).—*Cyanoisobutylaldehyde acetate*,



is a stable compound which boils, without decomposing, at 189° under ordinary pressure, and is insoluble in water (compare Abstr., 1895, ii, 257).

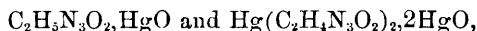
Acetylactylacetamide, $NHAc \cdot CO \cdot CHMe \cdot OAc$, constitutes the fraction which boils at about 178° , when the product of the action of acetic chloride on the lactic nitrile (*loc. cit.*) is distilled under a pres-

sure of 15 mm. It forms white, hygroscopic crystals which, when dry, melt at 73° . When dissolved in warm water, it forms a crystalline hydrate containing 1 mol. H_2O . It has none of the properties of cyanides, and yields no ammonia with aqueous potash in the cold. When heated in sealed tubes with water at 150° , it splits up into ammonium acetate and acetic and lactic acids.

Diacetyldilactamide, $NH(CO \cdot CHMe \cdot OAc)_2$, is obtained by the action of water at 0° on the crystalline product, $OAc \cdot CHMe \cdot CN + HCl$, obtained by the action of dry hydrogen chloride on cooled cyanisobutaldehyde acetate. It forms white, nacreous needles which melt at 110° , and, when heated with water at 150° , yields 3 mols. of acid. When dissolved in benzene, it forms crystals of the compound $NH(C_5H_7O_3)_2 + C_6H_6$, but when dissolved in acetic acid, its molecular weight is found to be 230 (calc. 245).

The formation of these amides is probably analogous to that of amides from nitriles by the action of water; the change is determined by the presence of a small quantity of hydrochloric acid, and takes place according to the equation, $R \cdot CN + Ac \cdot OH = R \cdot CO \cdot NHAc$.
C. H. B.

Biuret Reactions. By HUGO SCHIFF (*Ber.*, 1896, **29**, 298—303).—Biuret is best prepared by heating the liquid carbamide hydrochloride at 130° , and then separating the biuret from the potassium cyanate which is formed on treating the product with weak alcoholic potash. The following metallic derivatives have been examined and analysed. The *potash compound*, $C_2H_5N_3O_2 \cdot KOH$, crystallises in needles, and is decomposed by water and by the carbonic anhydride of the air. The compound with soda, $C_2H_5N_3O_2 \cdot NaOH$, has similar properties. Mercuric oxide forms two compounds,



both of which are obtained by adding mercuric nitrate to an aqueous solution of biuret.

Biuret unites with the soluble copper salts, forming light blue, crystalline compounds such as $CuSO_4 \cdot 2C_2H_5N_3O_2$, $CuCl_2 \cdot 2C_2H_5N_3O_2$, which are partially decomposed by water. The violet compound formed in the well known biuret reaction is best prepared by adding copper acetate solution to biuret, and then precipitating with alcoholic potash. It forms long, carmine-red needles, which may be preserved under weak alcoholic potash; this compound has the composition $2C_2H_5N_3O_2 \cdot 2KOH \cdot Cu(OH)_2$, the metals being probably united with the nitrogen of the amido-groups. Nickel salts behave towards biuret in the same manner as the copper salts, pale green compounds being produced, which form yellow solutions in aqueous potash. Cobalt salts also combine with biuret, but the products do not give a characteristic coloration with potash. The biuret reaction with potash and a copper or nickel salt, appears to be given by all such diamides as contain two $-CO \cdot NH_2$ groups united together, or with a single atom of carbon or nitrogen, or with several $-CO \cdot NH$ groups in an open chain. Thus malonamide and oxalyldiureide, $NH_2 \cdot CO \cdot NH \cdot NH \cdot CO \cdot NH_2$, give the reaction, whilst succinamide does not.
A. H.

Oximes of α -Halogenised Aldehydes, Ketones, and Acids: Oximido-acetic acids. By ARTHUR R. HANTZSCH and WILHELM WILD (*Annalen*, 1896, 289, 285—309).—The authors have found that hydroxylamine converts α -halogenised aldehydes and α -halogenised ketones of the type $R\cdot CHX\cdot CO\cdot R'$ into glyoximes of the general formula $R\cdot C(NO\cdot H)\cdot C(NO\cdot H)R'$, whilst α -halogenised acids yield α -oximido-acids of the type $R\cdot C(NO\cdot H)\cdot COOH$. Thus methylglyoxime has been obtained by the action of hydroxylamine on chloracetone, whilst dichlorethylic ether and amidothiazole have given rise to glyoxime; mono- and di-chloracetic acids yield oximidoacetic acid, whilst α -oximidopropionic and α -oximidobutyric acids are obtained from α -bromopropionic and α -bromobutyric acid respectively.

Oximidoacetic-acetic acid, $COOH\cdot CH\cdot N\cdot O\cdot CH_2\cdot COOH$ ("oximido-essigacetsäure"), is produced along with oximidoacetic acid when hydroxylamine acts on chloracetic acid; it crystallises from water in needles, and melts at 181° , yielding hydrogen cyanide. This acid is indifferent towards acetic anhydride and acetic chloride, but phosphorus pentachloride converts it into the oily *chloride*; neither ammoniacal silver nor Fehling's solution is reduced by the acid when boiled with it. The *ammonium* salt is a crystalline precipitate, and the *barium* salt, containing $1H_2O$, separates in small needles; the *silver* salt is crystalline, and the *amide* crystallises in leaflets and melts and decomposes at 214° . When the acid is reduced with hydriodic acid, glycocine is produced, and hot alkalis give rise to carbonic anhydride, hydrogen cyanide, and glycollic acid; it is indifferent towards boiling mineral acids, but at 140° , it is decomposed by 35 per cent. sulphuric acid into carbonic anhydride, ammonia, formic acid, and glycollic acid.

Oximidopropionic-acetic acid (compare Wolff, this vol., i, 88), $COOH\cdot CMe\cdot N\cdot O\cdot CH_2\cdot COOH$, is obtained by heating oximidopropionic and chloracetic acids with aqueous potash at 50 — 60° for three hours; it melts and decomposes at 130 — 132° . The acid is indifferent towards ammoniacal silver and Fehling's solution, and is not attacked by boiling alkalis and concentrated hydrochloric acid; the *silver* salt crystallises from hot water, and coloured precipitates are formed with copper and lead acetates, and ferric chloride. Amidopropionic acid is obtained on reducing the acid with hydriodic acid.

Normal benzaldoximido-acetic acid, $CHPh\cdot N\cdot O\cdot CH_2\cdot COOH$, is obtained by heating molecular proportions of the potassium derivative of benz-antialdoxime and potassium chloracetate in aqueous solution; it crystallises from hot water in long needles, and melts at 98° . It is indifferent towards Fehling's solution and boiling concentrated hydrochloric acid; alkalis convert it into benzonitrile and glycollic acid, whilst hydriodic acid at 100° gives rise to benzaldehyde, ammonia, and glycollic acid. The *potassium* salt contains $1H_2O$, and crystallises from water, whilst the *tin* salt separates in long needles; the *ethylic* salt crystallises in long needles, and melts at 59° .

Isobenzaldoximido-acetic acid, $\begin{matrix} CHPh \\ | \\ O \end{matrix} > N\cdot CH_2\cdot COOH$, is obtained from benzsynaldoxime and chloracetic acid; it crystallises in long needles, and melts at 183° , decomposing vigorously at this temperature.

Reduction with hydriodic acid gives rise to benzaldehyde and glycocine; it is readily oxidised by ferric chloride and Fehling's solution, yielding benzaldehyde, which is also formed under the influence of caustic potash and boiling hydrochloric acid.

Hydroxylamidoacetic acid (Traube, this vol., i, 9) is obtained along with benzaldehyde when isobenzaldoximidoacetic acid is treated with boiling hydrochloric acid. M. O. F.

Action of Hydroxylamine on Ethylic Succinate. By GIORGIO ERRERA (*Gazzetta*, 1895, 25, ii, 263—266).—By the action of hydroxylamine on ethylic succinate, Hantzsch and Urbahn (Abstr., 1895, i, 393) were unable to prepare pure succinylhydroxamic acid, but got a product which, on acetylation, yielded what they supposed to be a tetracetylsuccinylhydroxamic acid; this, however, the author finds to be the succinylacetoxylamine which he has recently described (this vol., i, 209). The behaviour of ethylic succinate towards hydroxylamine is, therefore, exactly similar to that of methylic phthalate (this vol., i, 222). W. J. P.

Synthesis in the Pentamethylene Series. By NICOLAI D. ZELINSKY and M. RUDSKY (*Ber.*, 1896, 29, 403—405).—Dimethylalipic acid, when distilled with calcium hydroxide, yields *dimethylketopentamethylene*; this boils at 145—147°, and does not combine with sodium hydrogen sulphite. The yield is 32 per cent. of the acid employed. When reduced by means of sodium in moist ethereal solution, a corresponding *alcohol* is formed; it boils at 154° (744 mm.), and has a sp. gr. = 0.9224 0°/0°. The yield is 75 per cent. of the ketone. By the action of hydriodic acid (sp. gr. = 1.96) at 100°, an oily *iodide* is formed, and this, by the further action of hydriodic acid at 220°, is converted into 1:3-*dimethylpentamethylene* boiling at 93° (743 mm.), the sp. gr. = 0.7543 at 20°/4°, the refractive index $n = 1.4130$ at 20°, and the molecular refractive power = 32.38, which agrees with the theoretical value for a saturated hydrocarbon. The compound has an odour of petroleum, is immediately coloured by bromine vapour, and quickly dissolves in fuming (yellow) nitric acid; this readily distinguishes it from the synthetical hexamethylene hydrocarbons which, at the ordinary temperature, are extremely stable towards nitric acid either alone or with sulphuric acid. J. B. T.

Syntheses in the Camphor and Terpene Series. By EMIL KNOEVENAGEL (*Annalen*, 1895, 289, 131—172; compare Abstr., 1895, i, 48, also Baeyer, Abstr., 1893, i, 258).—The author has synthesised numerous meta-alkyl derivatives of hydrogenised toluene by reducing certain cycloïd ketones which have been already described (*loc. cit.*); elimination of water from the phenols obtained in this way has given rise to dihydrotoluene derivatives. The carbon atoms are numbered

as indicated by the expression $\overset{7}{\text{C}}\overset{1}{\text{C}} < \overset{2}{\underset{\overset{6}{\text{C}}}{\text{C}}} \overset{3}{\text{C}} \overset{8}{\text{C}} \overset{9}{\text{C}} > \overset{4}{\text{C}}$, and reference is made to Δ_2 -ketotetrahydrobenzene derivatives as cyclohexenones.

Tetrahydrometacresol (methyl-1-cyclohexenol-5) is obtained by reducing methyl-1-cyclohexenone-5 with sodium and alcohol; it is a colourless, viscous oil, which boils at $175-176^{\circ}$, and is volatile in alcohol vapour and in steam. The sp. gr. = 0.9320 at 15° , and the refractive index $n_D = 1.4695$ at 15° , whence the molecular refraction $R = 33.48$. The substance is unsaturated, and gives rise to a liquid dibromide. The *acetyl* derivative boils at $188-189^{\circ}$, and the *urethane*, $C_{14}H_{17}O_2N$, obtained from phenylic isocyanate, melts at 90° ; the *chloride* is obtained by the action of phosphorus pentachloride, and decomposes slightly when boiled in a vacuum.

Tetrahydro-1:3:5-xylenol (dimethyl-1:3-cyclohexenol-5) is obtained from dimethyl-1:3-cyclohexenone-5, and boils at 187° under atmospheric pressure, and at 83° under a pressure of 15 mm.; the sp. gr. = 0.9056 at 15° and 0.9007 at 20.5° . The refractive index $n_D = 1.4539$ at 20.5° , whence the molecular refraction $R = 37.88$. The *dibromide* crystallises in colourless needles, and melts at 148° ; the *acetyl* derivative is a limpid, colourless liquid, which boils at $195-196^{\circ}$. The *urethane* melts at 107° , and the *chloride* is a highly refractive oil, which boils at $80-85^{\circ}$ under a pressure of 25 mm.; the *bromide* becomes brown and resinous in air, and the *iodide* boils at $110-115^{\circ}$ under a pressure of 25 mm.

Tetrahydro-1:3:5-carvacrol (methyl-1-isopropyl-3-cyclohexenol-5) is a colourless, viscous oil having the odour of peppermint; it boils at 112° , 125° , and 150° under pressures of 14 mm., 22 mm., and 65 mm. respectively, and under atmospheric pressure, it boils at 224° . The sp. gr. = 0.9090 at 15° , and the refractive index $n_D = 1.4684$ at 15° , whence the molecular refraction $R = 47.02$. The *acetyl* derivative is a colourless liquid having an agreeable odour, and boils at 228° ; the *methyl ether* boils at 122° under a pressure of 40 mm. The *chloride*, $C_{10}H_{17}Cl$, obtained from tetrahydrocarvacrol by the action of phosphorus pentachloride, is a colourless, highly refractive oil, which boils at $99-100^{\circ}$ under a pressure of 22 mm.; the *bromide* boils at 158° under a pressure of 24 mm.

Meta-isobutyltetrahydrometacresol (methyl-1-isobutyl-3-cyclohexenol-5) is obtained by reducing methyl-1-isobutyl-3-cyclohexenone-5 with sodium and alcohol; it boils at 119° and $127-129^{\circ}$ under pressures of 10 mm. and 20 mm. respectively. At 21.5° , the sp. gr. = 0.8909, and the refractive index $n_D = 1.4614$, whence the molecular refraction $R = 51.77$. The *acetyl* derivative boils at $132-134^{\circ}$ under a pressure of 18 mm., and the *methyl ether* at 112° under a pressure of 9 mm.; the *isopropyl ether* boils at 116° under a pressure of 10 mm.

Metahexyltetrahydrometacresol (methyl-1-hexyl-3-cyclohexenol-5) boils at $147-149^{\circ}$ under a pressure of 20 mm., and has the sp. gr. = 0.8840 at 21.5° , and the refractive index $n_D = 1.4617$ at 21.5° , whence the molecular refraction $R = 60.92$. The *acetyl* derivative boils at $154-156^{\circ}$ under a pressure of 22 mm., and the *methyl ether* at $135-136^{\circ}$ under a pressure of 10 mm.; the *isopropyl ether* has a disagreeable odour, and boils at $138-139^{\circ}$ under a pressure of 10 mm.

When the bromide of tetrahydrometacresol is distilled with 10 parts

of quinoline, dihydrotoluene is produced (compare Baeyer, *Annalen*, **155**, 271), and it is also obtained by treating tetrahydrometacresol with phosphoric anhydride. It boils at $106-107^{\circ}$, and has sp. gr. = 0.8088 at 15° , and 0.8017 at 18.3° , and the refractive index $n_D = 1.4460$ at 18.3° , whence the molecular refraction $R = 31.20$.

Dihydrometaxylene is obtained from tetrahydro-1 : 3 : 5-xenol by the action of phosphoric anhydride and by distilling the bromide with quinoline; it is also produced when the hydrochloride of tetrahydro-xylydine (Abstr., 1895, i, 52) is subjected to dry distillation, and by reducing symmetrical chlorodihydro-xylene (*loc. cit.*, 86). Dihydrometaxylene is a limpid, colourless liquid, which boils at 123° ; at 15° and 20.5° the sp. gr. = 0.7988 and 0.7948 respectively, whilst the refractive index $n_D = 1.4416$ at 20.5° , and therefore the molecular refraction $R = 35.92$. Alcoholic sulphuric acid (4 parts of alcohol and 1 of acid) develops a reddish-violet coloration, which subsequently becomes blue; when half the proportion of alcohol is employed, the liquid acquires a yellow tint, which changes to reddish-yellow, and finally becomes blue. These phenomena are attended with marked changes in the absorption spectra. Wallach has obtained a ketone isomeric with dimethyl-1 : 3-cyclohexenone-5, which yields dihydrometaxylene under the influence of zinc chloride (*Annalen*, **258**, 327), but the substance boils at $132-134^{\circ}$; both hydrocarbons, however, are converted into trinitrometaxylene (m. p. $180-181^{\circ}$) on nitration.

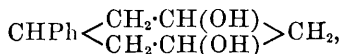
Dihydrometacymene (methyl-1-isopropyl-3-cyclohexadiene) is obtained by eliminating hydrogen bromide from the bromide of tetrahydro-1 : 3 : 5-carvacrol, or, more conveniently, by dehydrating this substance with phosphoric anhydride at 120° ; it boils at $171-172^{\circ}$, and has an odour recalling that of benzene, but like that of oranges, when diluted. The sp. gr. = 0.8170 at 15.5° , and the refractive index $n_D = 1.4564$ at 15.5° , whence the molecular refraction $R = 45.29$. The hydrocarbon reduces a cold solution of potassium permanganate, and takes up four atomic proportions of bromine. Alcoholic sulphuric acid (4 parts of alcohol and 1 of acid) develops a wine-red coloration with dihydrometacymene, gradually becoming violet-red; one-half the proportion of alcohol gives rise to a yellow tint, which becomes reddish-yellow, and subsequently violet, whilst the coloured liquids exhibit characteristic absorption spectra. The nitroschloride of dihydrometacymene melts at 150° . Repeated treatment of dihydrometacymene with bromine and quinoline has given rise to metacymene, identical with the hydrocarbon obtained by Wallach from fenchone (Abstr., 1895, i, 380); metacymene, from both sources, yields a yellow trinitro-derivative, which melts at 72° .

Meta-isobutyl dihydrotoluene (methyl-1-isobutyl-3-cyclohexadiene) is obtained from meta-isobutyltetrahydrometacresol by the action of phosphoric anhydride; it is a limpid, colourless liquid, which boils at 185° . The sp. gr. = 0.8089 at 21.5° , and the refractive index $n_D = 1.4501$ at 21.5° , whence the molecular refraction $R = 49.83$; characteristic colorations and absorption spectra are developed with alcohol and sulphuric acid. The hydrocarbon takes up four atomic proportions of bromine, but the product spontaneously loses hydrogen

bromide, and, when treated with quinoline, yields an oil, which probably contains meta-isobutyltoluene, because nitration gives rise to 2 : 4 : 6-trinitroisobutyltoluene, which has the odour of musk, and is isomeric with Baur's "artificial musk;" this compound, which crystallises from alcohol and melts at 124°, is also obtained from isobutylidihydrotoluene.

Metahexyldihydrotoluene (methyl-1-hexyl-3-cyclohexadiene) is produced when phosphoric anhydride acts on metabexyltetrahydrometacresol at 165°; it boils at 228—230°, has the sp. gr. = 0.8216 at 21.5°, and the refractive index $n_D = 1.4562$ at 21.5°, whence the molecular refraction $R = 58.90$. The hydrocarbon takes up four atomic proportions of bromine, and, on treating the product with quinoline, an oil containing metabexyltoluene is obtained; on nitration, this yields 2 : 4 : 6-trinitrometabexyltoluene, which melts at 131°, and has a feeble odour of musk.

Metaphenylhexahydroresorcinol (phenyl-5-cyclohexanediol-1 : 3),



is obtained by reducing phenyldihydroresorcinol with alcohol and sodium; it crystallises from water in lustrous leaflets, and melts at 157°. It is insoluble in benzene, and sparingly soluble in chloroform and ether; it does not dissolve more readily in potash than in water, and crystallises unaltered from the solution. When heated with phosphoric anhydride, it yields *dihydrodiphenyl*, which melts at 66—66.5°, and, although extremely soluble in alcohol and ether, crystallises well from these solvents; it is volatile in steam, and reduces a warm solution of potassium permanganate.

Diethyl 5-methyl-1 : 3-diketocyclohexane-4 : 6-dicarboxylate (Abstr., 1894, i, 577) is obtained from ethylic ethylidenemalonate and ethylic acetoacetate under the influence of sodium ethoxide. Hydrolysis and elimination of carbonic anhydride converts it into *metamethyldihydroresorcinol*, which crystallises from water, and melts at 125—126°; the aqueous solution is acidic, decomposing carbonates, develops a red coloration with ferric chloride, and reduces potassium permanganate. Metamethyldihydroresorcinol is a homologue of Merling's dihydroresorcinol (Abstr., 1894, i, 177), and, like that substance, yields a compound with formaldehyde; this crystallises from alcohol in lustrous needles, and melts at 152—153°. The *dioxime* of metamethyldihydroresorcinol melts at 155°. M. O. F.

The Cyclopentadiene of Coal Tar; the Indene of the Aliphatic Series. By GUSTAV KRAEMER and ADOLF SPILKER (*Ber.*, 1896, 29, 552—561).—The hydrocarbon of the formula C_9H_6 , which the authors obtained from coal tar (Abstr., 1891, 205), and to which Étard and Lambert, having isolated the substance from the condensation products of oil gas, have given the name pyropentylene (Abstr., 1891, 1085), has been submitted to further investigation; it is identical with the hydrocarbon described by Roscoe (*Trans.*, 1885, 47, 669), and, as the constitution is probably represented by the formula $\begin{array}{c} \text{C}_2\text{H}_2 \\ \text{C}_2\text{H}_2 \end{array} > \text{CH}_2$, the authors refer to it as the cyclopentadiene of coal tar.

The hydrocarbon boils at 41° (corr.) under a pressure of 760 mm., and has the sp. gr. = 0.80475 at $18.6^{\circ}/4^{\circ}$; it becomes resinous under the influence of alkalis and dilute acids, and is charred by concentrated sulphuric acid, the action of fuming nitric acid being so vigorous as to cause ignition. The refractive index $n_D = 1.4446$ at 18.6° , whence the molecular refraction $M = 36.45$, the value calculated for two ethylene linkings being $M = 36.04$.

Chlorocyclopentene, C_5H_7Cl , is obtained by saturating a solution of cyclopentadiene in chloroform, at low temperatures, with hydrogen chloride; it boils at 50° under a pressure of 40 mm., and has the sp. gr. = 1.0571 at $15^{\circ}/15^{\circ}$. It becomes resinous spontaneously, and loses hydrogen chloride; aqueous ammonia converts it into a substance resembling india-rubber, an unsaturated alcohol, and an unsaturated base, $C_5H_7NH_2$, which boils at $102-104^{\circ}$, and forms a *platinochloride*.

Trichlorocyclopentane, $CH_2<\begin{smallmatrix} CHCl \cdot CH_2 \\ | \\ CHCl \cdot CHCl \end{smallmatrix}>$, is produced by the action of chlorine on the monochloro-derivative at low temperatures; it boils at $195-197^{\circ}$, and has the sp. gr. = 1.3695 at $20^{\circ}/4^{\circ}$. The substance is indifferent towards cold, concentrated sulphuric and fuming nitric acids, and is slowly attacked by bases.

Tetrachlorocyclopentane, $C_5H_6Cl_4$, is obtained by leading chlorine into a solution of cyclopentadiene in chloroform at -15° ; it boils at 94° and 103° under pressures of 15 mm. and 25 mm. respectively, and has the sp. gr. = 1.423 at 15° .

Dibromocyclopentene, $C_5H_6Br_2$, is produced when bromine combines with cyclopentadiene at temperatures approaching -20° ; it crystallises in colourless prisms, and melts at $45-46^{\circ}$. The substance decomposes spontaneously, and is attacked vigorously by bases and concentrated acids.

Tetrabromocyclopentane, $C_5H_4Br_4$, is obtained from the foregoing compound by the action of bromine; it is a pale yellow liquid, having a sp. gr. = 2.5224 at $15^{\circ}/4^{\circ}$, and distils under diminished pressure without undergoing change.

Dicyclopentadiene, $CH<\begin{smallmatrix} CH \cdot CH \cdot CH \cdot CH \\ | \quad | \\ CH_2 \cdot CH \cdot CH \cdot CH_2 \end{smallmatrix}>CH$, is formed from cyclopentadiene by spontaneous change (compare Etard and Lambert; also Roscoe). It solidifies at 32.5° , and has the sp. gr. = 0.9766 at $33^{\circ}/4^{\circ}$; under pressures of 35 mm., 55 mm., and 760 mm., it boils at 88° , 95° , and 170° respectively, being in part converted into cyclopentadiene at the last named temperature. The refractive index $n_D = 1.5050$ at 35° , whence the molecular refraction $M = 68.44$, the calculated value being $M = 68.1$. The *nitrosochloride* melts at 182° , and is converted by piperidine into a *base*, which melts at 160° ; the *nitrosate* crystallises in lustrous prisms, and melts at 155° . Dicyclopentadiene forms additive compounds with halogens, but the derivatives are unstable; it immediately reduces a cold solution of potassium permanganate.

M. O. F.

Derivatives of Metaxylene. By A. KLAGES (*Ber.*, 1896, 29, 310-314).—Symmetrical chloroxylenes may be prepared from sym-

metrical xylidine by means of Sandmeyer's reaction; the product is identical with that previously obtained by Klages and Knoevenagel (Abstr., 1895, i, 86) from dimethylketotetrahydrobenzene. 5-Chlorometaxylenic-2-sulphonic acid forms colourless crystals melting at 52°, and is not hygroscopic. When fused with potash, it yields metaxyloquinol melting at 149—150°. The sulphonic acid is accompanied by a small amount of its anhydride. The *sulphonic chloride* forms large, rhombic crystals, and melts at 56—58°, whilst the *amide* crystallises in colourless needles, and melts at 191—192°. Symmetrical chloroxylenic is converted by fuming nitric acid and sulphuric acid into the 2:4:6-trinitro-compound, which melts at 218°. 4-Chloro-5-nitrometaxylene is prepared from 5-nitro-1:3:4-xylidine by Sandmeyer's reaction. It boils at 278°, melts at 52°, and, when reduced, yields 4-chloro-1:3:5-xylidine, which boils at 251°, and combines with the carbonic anhydride of the air; its *benzoyl derivative* melts at 128°. This base is usually accompanied by a *dichloro-1:3:5-xylidine*, which crystallises in colourless needles, melts at 72°, boils at 265—266°, and yields a *benzoyl derivative*, which melts at 158°. 4:5-Dichlorometaxylene can readily be obtained from 4-chloro-1:3:5-xylidine by means of Sandmeyer's reaction, and boils at 231—232°. 2:5-Dinitro-1:3:4-aceto-xylidide forms almost colourless needles melting at 226°, and dissolves in warm aqueous potash, forming an unstable potassium compound. 2:5-Dinitro-1:3:4-xylidine crystallises in yellow needles melting at 115°, which deflagrate when heated. This base can only be converted into the corresponding hydrocarbon with great difficulty. The resulting 2:5-dinitrometaxylene melts at 132°, and, when reduced, yields a base, the *benzoyl derivative* of which melts at 234°. 4-Chloro-2:5-dinitrometaxylene, obtained by means of Sandmeyer's reaction, forms yellow crystals, melts at 61°, and boils at 290—291°. On reduction, it yields the corresponding *base*, which boils at 280—281° and forms a *benzoyl derivative* melting at 164°. This base is readily converted, by treatment with ferric chloride and hydrochloric acid, into 4-chlorometaxyloquinone, which crystallises in compact needles melting at 218°. The formation of this substance proves that the base from which it is obtained, and the corresponding dinitro-compound, have the constitutions which have been assigned to them above.

A. H.

Phenylic Ethers of Nitro-compounds of Iron. By KARL A. HOFMANN and O. FRITZ WIEDE (*Zeit. anorg. Chem.*, 1896, **11**, 288—292; see also Abstr., 1895, ii, 451).—Dinitrosoferrophenyl mercaptide, $\text{Fe}(\text{NO})_2\text{SPh}$, which can only be obtained with difficulty by the method previously described, is easily prepared by adding the theoretical quantity of phenylhydrazine (7 mols.) to an alcoholic solution of potassium heptanitrosoferrothiosulphonic acid, $\text{Fe}_4(\text{NO})_7\text{S}_3\text{K}, \text{H}_2\text{O}$; the mixture being well cooled with ice, and allowed to remain two days. It crystallises in brown, lustrous plates, and melts at 179°. It is also obtained on gradually adding the theoretical quantity of diazobenzene nitrate to a solution of potassium heptanitrosoferrothiosulphonic acid in absolute alcohol, and cooling with ice. A determination of

the molecular weight by the cryoscopic method gave numbers agreeing with the formula $[\text{Fe}(\text{NO})_2\text{SPh}]_2$. E. C. R.

Action of Carbonyl Chloride on Dimethyl- and Diethyl-metamidophenol. By FRIEDRICH VON MEYENBURG (*Ber.*, 1896, **29**, 501--513).—Carbonyl chloride reacts with dimethyl- and diethyl-metamidophenol in the cold to form ethereal salts of carbonic and chloro-formic acids. At higher temperatures, red and violet colouring matters are produced. *Metadimethylamidophenylic carbonate*, $\text{CO}(\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{NMe}_2)_2$, is formed when an alkaline solution of metadimethylamidophenol is shaken with a solution of carbonyl chloride in benzene. It crystallises in long, feathery needles, melts at $137\text{--}138^\circ$, and boils at 265° (pressure = 15 mm.). It dissolves in moderately strong acids, but is insoluble in alkalis and water; it is not affected by aqueous potash at 100° , but is hydrolysed by alcoholic potash, &c. The salts are unstable, and readily lose a portion of their acid; the *hydrochloride* crystallises in flat needles, and melts and decomposes at 205° ; the *picrate* melts at 162° , whilst the *platinochloride* forms golden-yellow granules, and is very unstable. *Metadimethylamidophenylic chloroformate*, $\text{COCl}\cdot\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{NMe}_2$, is formed when dimethylamidophenol in benzene solution is added to an excess of carbonyl chloride dissolved in the same solvent. It is obtained as a syrup, which decomposes when preserved, and has not been analysed. Water decomposes it with evolution of carbonic anhydride.

Metadiethylamidophenylic carbonate crystallises in colourless prisms melting at 67° , and boils at 292° (pressure = 5 mm.). The salts are less stable than those of the dimethyl compound. The *hydrochloride* melts and decomposes at 205° , and the *hydriodide* melts at 201° . *Metadiethylamidophenylic chloroformate*, forms a syrup which partially solidifies when preserved at 0° for some days. *Metadiethylamidophenylic acetate* is a colourless oil which boils at $160\cdot5^\circ$ (pressure = 5 mm.).

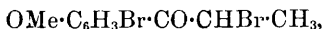
When the dialkylamidophenols are heated with carbonyl chloride at 160° , red colouring matters are formed, which are probably derivatives of triphenylmethane, and have the general formula $\text{NR}_2\cdot\text{C}_6\text{H}_3(\text{OH})\cdot\text{C}\begin{smallmatrix} \text{C}_6\text{H}_3(\text{NR}_2\text{Cl}) \\ \text{C}_6\text{H}_3(\text{NR}_2) \end{smallmatrix}\text{--O}$. These substances closely resemble the pyronines in colour and absorption spectrum, and the author proposes to call them *phosgenepyronines*. The red colouring matter from diethylamidophenol forms a violet *sodium salt*, the solution of which is decolorised on heating, the red colouring matter being precipitated. The base of the colouring matter appears to exist in two forms, for when the violet solution of the sodium salt is shaken with toluene, a violet solution is obtained, whereas the base precipitated by boiling from the alkaline solution dissolves in toluene, forming a reddish-yellow solution. Both solutions yield the original colouring matter when extracted with dilute acid. When the dialkylamidophenols are heated with carbonyl chloride at 100° , violet colouring matters are formed, the colour bases of which also appear to exist in two forms. These substances could not be analysed.

A. H.

Derivatives of Isanethoil. By CARL HELL and CARL GAAR (*Ber.*, 1896, **29**, 344—352).—Isanethoil, $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CH}:\text{CH}_2$, was obtained by fractionating essence of tarragon, and formed the chief constituent of the fraction boiling at $208\text{--}214^\circ$, which was about one-half of the whole. It was brominated in cooled ethereal solution, when a compound, $\text{OMe}\cdot\text{C}_6\text{H}_3\text{Br}\cdot\text{CH}_2\cdot\text{CHBr}\cdot\text{CH}_2\text{Br}$, melting at 62.4° , was obtained; it was not found possible to add bromine without substitution occurring at the same time, nor was it possible to introduce more than 1 bromine atom into the C_6H_4 group. When this bromine derivative is oxidised with chromic acid in acetic acid solution, it yields a *tribromo-ketone*, $\text{OMe}\cdot\text{C}_6\text{H}_3\text{Br}\cdot\text{CO}\cdot\text{CHBr}\cdot\text{CH}_2\text{Br}$, melting at 103.5° ; whereas the isomeric bromide from anethoil,

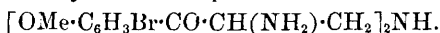


yields only a dibromo-ketone, which must have the formula



for had it been the other CHBr -group that underwent oxidation, there would be no reason why the same CHBr -group should not undergo oxidation in the case of the iso-compound. It would seem therefore that it is always the group next to the benzene ring which is oxidised, the position of the bromine atoms being without influence.

This ketone is oxidised by permanganate to bromanistic acid; no acetic acid is formed. With alcoholic ammonia at 110° , it forms a compound, apparently of the composition



With alcoholic potassium acetate, it yields a compound, possibly $\text{OMe}\cdot\text{C}_6\text{H}_3\text{Br}\cdot\text{CO}\cdot\text{CH}(\text{OAc})\cdot\text{CH}_2\cdot\text{OAc}$. With sodium ethoxide, it does not yield an ethoxy-derivative; bromanistic acid is formed. These last experiments were performed with very small quantities of substance, and great importance cannot be attached to the results.

C. F. B.

Constitution of Phenoquinone. By C. LORING JACKSON and GEORGE OENSLAGER (*Amer. Chem. J.*, 1896, **18**, 1—22).—The theoretical speculations in this paper have already appeared (*Abstr.*, 1895, i, 513).

Dichlorodiamyloxyquinone diethylhemiacetal, $\text{C}_6\text{Cl}_2(\text{OH})_2(\text{OC}_2\text{H}_5)_4$, (compare this vol., i, 19), is prepared, in the form of its *sodium* salt, by stirring together finely powdered dichlorodiphenoxyquinone (4 grams) and a solution of sodium (1 gram) in amylic alcohol (25 c.c.); the salt remains dissolved, and is precipitated by the addition of ethylic alcohol. The hemiacetal is obtained by treating the sodium salt with acetic acid; it is a white solid, insoluble in water, and rapidly decomposes, yielding a yellow oil. When the sodium salt is warmed with strong hydrochloric acid, *dichlorodiamyloxyquinone*, $\text{C}_6\text{Cl}_2(\text{OC}_2\text{H}_5)_2\text{O}_2$, is deposited as a yellow oil, which crystallises with difficulty from acetic acid in irregular, yellowish-red plates; it melts at 53° , and is soluble in most organic solvents. Reduction with zinc dust and glacial acetic acid converts this quinone into *dichlorodiamyloxyquinol*, $\text{C}_6\text{Cl}_2(\text{OC}_2\text{H}_5)_2(\text{OH})_2$, which crystallises in long, thin, white plates, melts at 128° , and dissolves freely in ether, benzene, chloroform,

acetone, glacial acetic acid, and carbon bisulphide, slightly in light petroleum, and not at all in water.

It was found that dichlorodibenzylloxyquinone dibenzylhemiacetal is white, although, on account of its great instability, no attempt was made to analyse it.

Dichlorodibenzylloxyquinone, $C_6Cl_2(OC_7H_7)_2O_2$, is prepared by mixing a solution of sodium (0.5 gram) in benzylic alcohol (4 c.c.) with absolute ether (150 c.c.), and adding chlorodiphenoxyquinone (2 grams), washing the separated mass with ether, adding it to water, and crystallising the oil, which floats to the surface, from a mixture of benzene and alcohol. It forms long, slender, red plates, melts at 142° , and dissolves freely in alcohol, acetone, benzene, glacial acetic acid, and ethylic acetate, but not at all in ether, light petroleum, or water. By reduction, the quinone yields *dichlorodibenzylloxyquinol*, $C_6Cl_2(OC_7H_7)_2(OH)_2$, which crystallises in white needles, melts at $122-123^\circ$, and is freely soluble in alcohol, ether, benzene, glacial acetic acid, and carbon bisulphide, but only slightly in light petroleum and not at all in water.

Full details of the preparation of the blue disodium salt from quinone and sodium phenoxide, and from phenoquinone and sodium β -naphthoxide (Abstr., 1895, i, 513), are given; the salt is very unstable, ignites spontaneously in the water oven, and is decomposed by water.

Quinonedinaphthylhemiacetal, $C_6H_4O_2(C_{10}H_7OH)_2$, is prepared by mixing benzene solutions of quinone (1.5 grams) and β -naphthol (3 grams) and evaporating; it crystallises in thin, brown, rectangular plates, melts at 82° , and dissolves freely in ether, chloroform, benzene, glacial acetic acid, and ethylic acetate, but only sparingly in light petroleum; the sodium salt is described.

Thymoquinonequinolhemiacetal, $C_{10}H_{12}O_2C_6H_4(OH)_2$, from hydroquinone and thymoquinone in ethereal solution, crystallises in dark brown, rectangular prisms with a green reflection; it melts at $136-137^\circ$, and dissolves easily in various solvents, nearly all of which, however, decompose it, dissolving one or other of its constituents.

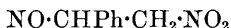
The reaction between thymoquinol and quinone produces quinhydrone. The authors point out that quinhydrone has no sharp melting point, but begins to decompose at 163° , the change being complete at 170° , when a sublimate of quinone, and, above that, one of quinol, is noticed in the melting tube.

A list of substances analogous to phenoquinone, which have been prepared from quinones, is given, together with references to the literature of the subject.

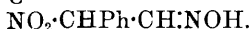
A. G. B.

α - and β -Cinnamene Nitrosite. By E. A. SOMMER (Ber., 1896, 29, 356-360; compare Abstr., 1895, i, 456).—The molecular weight of the β -nitrosite agrees with the formula $C_8H_8N_2O_3$, that of the α -compound could not be determined on account of its insolubility and instability; when heated, it decomposes into phenylnitroethylene, benzonitrile, nitric oxide, carbonic anhydride, and water; it is, therefore, probably more complex than the β -derivative, which melts with-

out decomposition. The latter is not changed by distillation with steam; when heated alone, it yields benzonitrile, nitric oxide, carbonic anhydride, water, and, in traces, ammonia. When heated with water under pressure during five hours, both compounds yield benzoic acid, benzonitrile, carbonic anhydride, water, ammonia, and nitrogen; probably the primary products are benzonitrile, carbonic anhydride, and hydroxylamine, and these interact with the result stated. By the action of nitrous acid on cinnamene, two compounds,



and $\text{NO}_2\cdot\text{CHPh}\cdot\text{CH}_2\cdot\text{NO}$, might be formed, and by the combination of 2 mols. of these, three substances are theoretically possible; from its decomposition products, the α -nitrosite probably has the formula $\text{O}-\text{N}-\text{CHPh}\cdot\text{CH}_2\cdot\text{NO}\cdot\text{O}$, the β -compound being



Both the other double molecular compounds appear to be formed, the

one, $\text{O}-\text{N}-\text{CHPh}\cdot\text{CH}_2\cdot\text{NO}-\text{O}$, readily yields phenylnitroethylene

nitric oxide and hydrogen, the second, $\text{O}-\text{NO}\cdot\text{CHPh}\cdot\text{CH}_2\cdot\text{N}-\text{O}$, is

probably unstable, and should easily change into the β -nitrosite, the decomposition products of which were isolated. The β -nitrosite forms a *silver* salt, and crystallises from boiling concentrated hydrochloric acid in colourless, lustrous needles. Angeli states that when boiled with mineral acids, it is converted into a ketone or aldehyde. The α -nitrosite combines with aniline, forming a crystalline base, $\text{C}_{14}\text{H}_{14}\text{N}_2\text{O}_2$; the *hydrochloride*, $\text{C}_{14}\text{H}_{14}\text{N}_2\text{O}_2\cdot\text{HCl}$, is deposited in white crystals with a pale, rose-coloured reflex; it decomposes when exposed to the air.

J. B. T.

Action of Nitrous acid on Safrole. By ANGELO ANGELI and ENRICO RIMINI (*Gazzetta*, 1895, **25**, ii, 188—213).—A good yield of safrole α -nitrosite may be obtained by slowly adding dilute sulphuric acid to potassium nitrite solution covered with a solution of safrole in light petroleum, and recrystallising the precipitate; on boiling with alcohol, it yields the β -nitrosite, which is readily converted into hydroxylamine and *nitropiperonylacetone*,



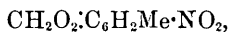
by boiling with dilute sulphuric acid. This ketone crystallises in colourless scales melting at 86° , and, when heated with hydroxylamine hydrochloride and sodium carbonate solution, yields *homopiperonyloxamic acid*, $\text{CH}_2\text{O}_2\cdot\text{C}_6\text{H}_3\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{OH}$; this crystallises in minute, white needles, melting and decomposing at 166° , is very soluble in alcohol, and is converted into homopiperonylic acid and hydroxylamine on boiling with dilute sulphuric acid. On heating nitropiperonylacetone with hydroxylamine hydrochloride in presence of but little alkali, safrole β -nitrosite is regenerated.

That nitropiperonylacetone, which readily reduces Fehling's and ammoniacal silver nitrate solutions, is not an aldehyde, but has the

constitution assigned above, is evident from the fact that it yields homopiperonylic acid on oxidation with potassium permanganate. On treating it with potassium nitrite and distilling the product in a current of steam, piperonylnitrile, melting at 94° , is obtained, and, on treating nitropiperonylacetone with bromine in acetic acid solution, *bromopiperonylnitroacetone*, $\text{CH}_2\text{O}_2\cdot\text{C}_6\text{H}_2\text{Br}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CH}_2\cdot\text{NO}_2$, is formed; it melts at 115° , is soluble in acetone or ethylic acetate, and on oxidation with alkaline permanganate yields *bromohomopiperonylic acid*, $\text{CH}_2\text{O}_2\cdot\text{C}_6\text{H}_2\text{Br}\cdot\text{CH}_2\cdot\text{COOH}$; this crystallises in lustrous needles melting at $190-191^{\circ}$.

Bromopiperonylnitrile, $\text{CH}_2\text{O}_2\cdot\text{C}_6\text{H}_2\text{Br}\cdot\text{CN}$, is obtained by distilling the product obtained by heating bromopiperonylnitroacetone with sodium nitrite solution in a current of steam; it crystallises in minute, white needles melting at 106° , is very soluble in benzene, acetone, or ethylic acetate, and gives a deep yellow coloration with sulphuric acid.

Nitropiperonylnitroacetone, $\text{CH}_2\text{O}_2\cdot\text{C}_6\text{H}_2(\text{NO}_2)\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CH}_2\cdot\text{NO}_2$, prepared by direct nitration, is crystalline, and melts at 170° ; it gives a beautiful, blue coloration with potash, and, when the product is distilled in a current of steam, a yellow *nitropiperonylmethane*,



melting at 83° , is obtained.

Piperonylamidoacetone, $\text{CH}_2\text{O}_2\cdot\text{C}_6\text{H}_3\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CH}_2\cdot\text{NH}_2$, may be prepared by reducing nitropiperonylacetone with tin and hydrochloric acid; the *hydrochloride*, $\text{C}_{10}\text{H}_{11}\text{NO}_3\cdot\text{HCl}$, crystallises in flattened needles, melting and decomposing at 198° , and reduces Fehling's solution, whilst the yellow *picrate*, $\text{C}_{10}\text{H}_{11}\text{NO}_3\cdot\text{C}_6\text{H}_2(\text{NO}_2)_3\cdot\text{OH}$, melts and decomposes at 160° . The free base is not obtained by adding ammonia to its hydrochloride, but a condensation product, *paradihomopiperonylpyrazine*, $\text{CH}_2\text{O}_2\cdot\text{C}_6\text{H}_3\cdot\text{CH}_2\cdot\text{C}\begin{smallmatrix} \text{CH}\cdot\text{N} \\ \text{N}\cdot\text{CH} \end{smallmatrix}\text{C}\cdot\text{CH}_2\cdot\text{C}_6\text{H}_3\cdot\text{CH}_2\text{O}_2$, is formed; it crystallises in small needles, melts at $155-156^{\circ}$, and gives a violet coloration with sulphuric acid.

Diazopiperonylacetone, $\text{CH}_2\text{O}_2\cdot\text{C}_6\text{H}_3\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CH}\begin{smallmatrix} \text{N} \\ \text{N} \end{smallmatrix}$, is obtained as a yellow oil, together with its decomposition product, homopiperonylic acid, by treating piperonylamidoacetone hydrochloride with sodium nitrite solution; it is decomposed by mineral acids with evolution of nitrogen.

W. J. P.

Synthesis of Aromatic Selenium Compounds by means of Aluminium Chloride. By FRIEDRICH KRAFFT and A. KASCHAU (*Ber.*, 1896, **29**, 428-435).—A refutation of Chabrié's criticism (*Abstr.*, 1895, i, 413). The authors have obtained pure phenylic selenide by acting on selenium tetrachloride with benzene in the presence of aluminium chloride at a low temperature and fractionating the product. Diphenylic diselenide is, however, formed at the same time, and the method previously described (*Abstr.*, 1894, i, 89) of preparing the selenide is far more convenient. Chabrié never obtained the selenide pure; it was mixed with diselenide, and this he

mistook for hydroselenide. Further, what he described as selenoxide was, in reality, impure selenide. C. F. B.

Thianthrene (Diphenylene Bisulphide), $C_{12}H_8S_2$, and Selenanthrene. I. By FRIEDRICH KRAFFT and ROBERT E. LYONS (*Ber.*,

1896, **29**, 435—443).—Thianthrene, $C_6H_4<\underset{S}{\overset{S}{S}}>C_6H_4$, has been obtained by many observers and by various reactions; it is best prepared by slowly adding a benzene solution of sulphur dichloride to a cooled solution of aluminium chloride in benzene; it melts at 158—159°, and boils at 210° under 15 mm. pressure. *Ditolylene bisulphide* was prepared in a similar manner from toluene; it melts at 117—118°, and boils at 228—231° under 14 mm. pressure. Thianthrene is oxidised by boiling with nitric acid of sp. gr. 1·2 to *thianthrene dioxide*, $C_6H_4<\underset{SO}{\overset{SO}{S}}>C_6H_4$. This melts at 229°, is converted by reducing agents into thianthrene, and sublimes at 272—274° under 13 mm. pressure, undergoing at the same time a molecular transformation into *thianthrenemonosulphone (diphenylene sulphide sulphone)*, $C_6H_4<\underset{-S-}{\overset{SO_2}{S}}>C_6H_4$, which melts at 279°, and is converted by oxidation with chromic acid in boiling acetic acid solution into the disulphone, $C_6H_4<\underset{SO_2}{\overset{SO_2}{S}}>C_6H_4$. This last substance yields thianthrene and sulphurous anhydride when it is heated with sulphur.

Phenylic sulphide can also be oxidised readily to the sulfoxide by boiling it with nitric acid of sp. gr. 1·1. The sulfoxide boils at 199—200° under 10 mm., at 210° under 15 mm., and at about 340° under ordinary pressure, a slight decomposition taking place in the last case. When it is gently boiled for some time in an atmosphere of carbonic anhydride, the sulphide is regenerated; in this respect it analogous to the selenoxide (this vol., i, 304). C. F. B.

Thianthrene and Selenanthrene, $C_{12}H_8Se_2$. II. By FRIEDRICH KRAFFT and A. KASCHAU (*Ber.*, 1896, **29**, 443—445).—*Selenanthrene*

(*diphenylene diselenide*), $C_6H_4<\underset{Se}{\overset{Se}{S}}>C_6H_4$, is formed by gently heating diphenylenedisulphone (preceding abstract) with selenium in an atmosphere of carbonic anhydride; a steady evolution of sulphurous anhydride accompanies the reaction. It melts at 180—181°, and boils at 223° under 11 mm. pressure. When it is heated at 60—70° with nitric acid of sp. gr. 1·4, the solution, on cooling, yields crystals, which liberate iodine from potassium iodide and have a composition corresponding with the formula $C_{12}H_8Se_2, 2HNO_3$; when these crystals are treated with aqueous soda in the cold, and the mixture is saturated with carbonic anhydride and then evaporated under diminished pressure, alcohol extracts *selenanthrene dioxide*, $C_6H_4<\underset{SeO}{\overset{SeO}{S}}>C_6H_4$, from the residue. This melts at 270°, but at the same time loses oxygen and regenerates selenanthrene. C. F. B.

Nitramines. By ANTOINE P. N. FRANCHIMONT and H. VAN ERP (*Rec. Trav. Chim.*, 1895, **14**, 235—251; compare *Abstr.*, 1895, i, 587).—*Methyloctylnitramine*, $C_8H_{17}NMe \cdot NO_2$, obtained by heating octylic iodide (31 grams), methylnitramine (10 grams), potassium hydroxide (10 grams), and absolute methylic alcohol (30 grams) for three days on a water bath, and purified by fractional distillation under diminished pressure, forms a slightly yellow liquid, and distils at 164.5° under 17.5 mm. pressure. When heated with aqueous potash at 160° , it is not appreciably acted on.

Methylbenzylnitramine, $CH_2Ph \cdot NMe \cdot NO_2$, after distillation in a vacuum and pressing between filter paper, forms a crystalline mass, which melts at 22.2° and has a slightly aromatic smell. When heated at 150 — 160° with aqueous potash, it is decomposed into benzaldehyde, methylamine, nitrous acid, and a small quantity of benzoic acid.

Methylorthonitrobenzylnitramine crystallises in yellowish needles and melts at 87° . It is only sparingly soluble in ether and light petroleum, but readily in alcohol, chloroform, and benzene. When heated with aqueous potash for seven hours at 150° , it yields methylamine and benzoic acid.

Methylparanitrobenzylnitramine melts at 70 — 71° , and is decomposed when heated with potash at 140 — 150° , yielding the same compounds as the ortho-compound.

When dimethylnitramine itself is heated with aqueous potash, it yields methylamine, formaldehyde, methylic alcohol, formic acid, and nitrous acid.

The authors think that the decomposition by alkali is first preceded by intramolecular change, $(CH_3)_2N \cdot NO_2 \rightarrow CH_3 \cdot NH \cdot CH_2 \cdot NO_2$. This, under the influence of the alkali, yields $CH_3 \cdot NH_2$ and $OH \cdot CH_2 \cdot NO_2$, the latter being further decomposed into formaldehyde and nitrous acid (compare Bamberger, *Ber.*, **26**, 490). J. J. S.

Action of Sodium on Aromatic Nitriles. By C. A. ALFRED LOTTERMOSER (*J. pr. Chem.*, 1896 [2], **53**, 143—144).—The author has continued the study of the reactions between aromatic nitriles, aromatic amines and sodium, in benzene, first noticed by Walther (*Abstr.*, 1894, i, 503), and has prepared the following amidines: Orthotolylbenzenylamidine, paratolylbenzenylamidine, phenacetophenylamidine, orthotoluphenylamidine, paratoluphenylamidine, α -naphthophenylamidine, β -naphthophenylamidine. By the action of sodium on benzonitrile in benzene, a compound, which is probably dihydrotetraphenyltriazine, has been prepared. This investigation is proceeding. A. G. B.

Quantitative Reduction of the Nitro-group to the Hydroxylamine-group. By HANS WISLICENUS (*Ber.*, 1895, **29**, 494—496).—Nitrobenzene is quantitatively reduced to phenylhydroxylamine when it is dissolved in ether, and treated with amalgamated aluminium filings, water being gradually added, and the mixture cooled by ice. A vigorous action occurs, which should be so regulated that the ethereal solution boils freely. Nitroacetophenone also undergoes reduction under the same conditions (compare Wislicenus and Kaufmann, *Abstr.*, 1895, i, 437, 634). A. H.

Chemistry of the Diazo-compounds. By EUGEN BAMBERGER (*Ber.*, 1896, 29, 446—473).—The author still maintains, in opposition to Hantzsch, that the metallic, normal, and iso-diazo-derivatives are structurally, and not merely geometrically, isomeric, and he denotes them respectively by the formulæ $\text{Alph}\cdot\text{N}(\text{:N})\cdot\text{OM}$ and $\text{Alph}\cdot\text{N}:\text{N}\cdot\text{OM}$ [Alph = an aromatic radicle, such as C_6H_5 , $\text{C}_6\text{H}_4\text{Me}$, &c.; M = a metal]; for the salts of diazobenzene with acids he adopts Hantzsch's name of alphyldiazonium salts. In proof of the difference of structure alluded to, further experimental evidence is brought forward. The alkaline normal diazo-salts react with aliphatic alcohols in the cold, yielding diazo-ethers, $\text{Alph}\cdot\text{N}_2\cdot\text{OMe}$, &c.; the iso-salts do not behave in this way. Again, the normal salts are scarcely attacked by sodium amalgam, whereas the iso-salts are readily reduced to hydrazines. But an even more striking difference is seen in the behaviour of these salts with regard to acids. These liberate from the iso-salts the isodiazo-hydroxides, which form either oils or crystals, are colourless, or pale yellow when nitro-groups are present, and are readily dissolved by alkalis with re-formation of the iso-salt; *paranitroisodiazo benzene hydroxide*, $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{OH}$, has actually been analysed, but the experimental data are to be given in a future paper. From the normal salts, on the other hand, acids at a low temperature liberate diazo-anhydrides; these are bright yellow, extremely unstable substances; when placed on a porous plate, they explode spontaneously as soon as they become even approximately dry; diazobenzene anhydride even exploded once while still in the solution at a temperature of -18° , and some moist diazotoluene anhydride at a temperature of 0° was exploded by the concussion due to the explosion, at a distance of 5 ft., of a small sample of the dry substance. They also readily become transformed into diazoamido-compounds. With alkalis, they re-form the colourless normal diazo-salts, whilst with acids, they give the colourless diazonium salts. (In this connection it is interesting to remember that the colourless ethobromide of papaverine, $\text{C}_{20}\text{H}_{21}\text{NO}_4\cdot\text{EtBr}$, yields an oxide, $(\text{C}_{20}\text{H}_{21}\text{NO}_4\cdot\text{Et})_2\text{O}$, which is bright yellow; and also that the oxides of several metals—lead, for example—are coloured, whilst the salts of the same metals are colourless).

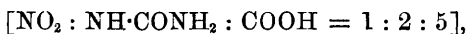
Parachlorodiazobenzene anhydride, $(\text{C}_6\text{H}_4\text{Cl}\cdot\text{N}_2)_2\text{O}$, was the most stable of the compounds prepared; it was even possible to analyse it, and with it the reactions of the diazo-anhydrides were studied in greater detail. The other anhydrides prepared were those of paradiazotoluene, diazobenzene, metachlorodiazobenzene, para- and meta-bromodiazobenzene and para- and meta-nitrodiazobenzene; their reactions, so far as they could be studied, resembled those of the anhydride of parachlorodiazobenzene. This yields diazo-ethers with aliphatic alcohols; with benzene, chlorodiphenyl, $\text{C}_6\text{H}_4\text{ClPh}$; with aniline, yellow *chlorodiazoamidobenzene*, $\text{C}_6\text{H}_4\text{Cl}\cdot\text{N}_2\cdot\text{NHPh}$, melting at 86° , not prepared before (with ammonia, paradiazotoluene anhydride yields bistoluene diazoimide, $(\text{C}_6\text{H}_4\text{Me}\cdot\text{N}_2)_2\text{NH}$); with bromine, the diazoperbromide; with phenylic hydrosulphide, apparently phenylthiodiazobenzene, $\text{C}_6\text{H}_4\text{Cl}\cdot\text{N}_2\cdot\text{SPh}$; with iodine, paraiodochlorobenzene, together with some chlorobenzene.

The general method of preparing a diazoanhydride is first to obtain the normal potassium diazo-salt by slowly adding a diazotised solution of the base to a cooled, very strong solution of potassium hydroxide in water, or mixture of the hydroxide with water; the salt is then drained with the aid of a filter pump and preserved in a dry atmosphere free from carbonic anhydride. A concentrated aqueous solution or the salt suspended in water is then treated, at 0° or in a freezing mixture, with 50 per cent. acetic acid, when the diazo-anhydride separates out in yellow, crystalline flakes.

The normal potassium diazo-salts are very readily converted into the iso-salts; at $120-130^{\circ}$, the conversion is complete in 20—30 minutes, and the carbonic anhydride of the air effects the conversion at the ordinary temperature. The presence of alkali does not favour, but even retards, this transformation; when iso-salts are obtained from normal salts by heating them with alkali, which is the usual method of preparation, it is the rise of temperature that brings about the transformation; the alkali only acts by preventing other decompositions taking place as a result of the rise in temperature.

C. F. B.

Constitution of Azimides [Azoimides]. By THEODOR ZINCKE and BRUNO HELMERT (*J. pr. Chem.*, 1896, [2], 53, 91—99).—Griess based his conclusion that the azoimides are correctly represented as derivatives of the compound $C_6H_4<\overset{N}{\underset{N}{|}}>NH$ on the fact that he obtained the same azimidobenzoic acid whichever of the two nitrouramidobenzoic acids, $[NO_2 : NH \cdot NHCONH_2 : COOH = 1 : 2 : 4]$ or



he heated with potash solution; furthermore, the same azimido-uramidobenzoic acid was formed when the nitro-acids were reduced and diazotised (Abstr., 1883, 56). It may well be, however, that the similarity between these azimido-acids is so great that even Griess may have been unable to differentiate them. In view of this possibility, the authors decided to repeat Griess' work, and will publish their results, but for the present they content themselves with saying that the characterisation of the azimido-acids in question is so difficult that their identity is hard to establish. It has been possible to obtain two azoimides of the general form $X \cdot C_6H_3N_3R$, which are undoubtedly isomerides, and this fact is only explicable on the supposition that Kekulé's typical formula, $C_6H_4<\overset{N}{\underset{NH}{|}}>N$, for the azoimides is correct.

The azoimide, $EtO \cdot C_6H_3<\overset{N}{\underset{NPh}{|}}>N$ [$EtO : NPh = 1 : 4$] is prepared by passing through a number of intermediate products, from metadinitrodiphenylamine (compare Nietzki, this vol., i, 164; the authors find that the azoimide $NO_2 \cdot C_6H_3N_3Ph$, melts at 167° , not at 107° as stated by Nietzki); it crystallises from all solvents in curved needles, and melts at 99° ; a saturated alcoholic solution yields no crystals when in contact with the 1 : 3-compound de-

scribed below, and when it does yield crystals these melt at 99° . The methiodide melts and decomposes at 211° .

The azoimide $\text{EtO}\cdot\text{C}_6\text{H}_3\cdot\text{N}^{\text{NPh}}\text{N} \text{ [OEt : NPh = 1 : 3]}$, is prepared from hydroxyazobenzene, through a number of intermediaries, and has been already described by Jacobsen and Fischer (Abstr., 1892, 840); it crystallises from all solvents except glacial acetic acid, in laminæ, and melts at $107\text{--}108^{\circ}$; a saturated alcoholic solution of it yields no crystals when in contact with the 1 : 4-derivative already described, but laminæ, melting at $107\text{--}108^{\circ}$ afterwards separate. The methiodide melts and decomposes at 177° .

A mixture of these isomerides, crystallises from alcohol, and melts at $70\text{--}75^{\circ}$.

The methylnitrazimidobenzene, $\text{NO}_2\cdot\text{C}_6\text{H}_3\cdot\text{N}_3\cdot\text{CH}_3$, prepared from nitrazimidobenzene, $\text{NO}_2\cdot\text{C}_6\text{H}_3\cdot\text{N}^{\text{NH}}\text{N}$, was found to melt at 161° and to be identical with that obtained by heating chlorodinitrobenzene, $[\text{Cl} : (\text{NO}_2)_2 = 4 : 1 : 3]$, with methylamine, reducing the dinitromethylaniline, which is formed, and diazotising the nitramidomethylaniline obtained by the reduction. Since the methyl-nitrazimidobenzene prepared in this way must contain the NCH_3 in the para-position relatively to the nitro-group, it follows that the nitrazimidobenzene must contain the NH -group in the para-position relatively to the nitro-group. No isomeride of the nitrazimidobenzene or of the methyl derivative was obtained, and the authors deem it possible that compounds of the type $\text{X}\cdot\text{C}_6\text{H}_3\cdot\text{N}_3\cdot\text{H}$ can exist in one form alone.

A. G. B.

Reduction of Unsaturated Aromatic Ketones and their Conversion into Coumarane Derivatives.

By CARL D. HARRIES and GEORGE J. BUSSE (*Ber.*, 1896, 29, 375—380; compare Abstr., 1895, i, 279).—*Propyl orthohydroxystyryl ketone* (propylorthocoumaroketone), $\text{HO}\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{CH}\cdot\text{COPr}^a$, is prepared by the condensation of salicylaldehyde and methyl propyl ketone in presence of soda; it crystallises from dilute alcohol, is somewhat soluble in warm water, and melts at 116° . At the boiling point, 1 c.c. of alcohol dissolves 1 gram of the ketone. The yield is 80 per cent. of the aldehyde employed. The *phenylhydrazone*, $\text{HO}\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{CH}\cdot\text{CPr}^a\cdot\text{N}_2\cdot\text{HPh}$, crystallises in small, yellow prisms, melts at 119° , and resembles the ketone in solubility. *Propyl orthohydroxyphenylethyl ketone* (propyldihydroorthocoumaroketone), $\text{HO}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{COPr}^a$, is obtained by the action of sodium amalgam on the unsaturated ketone; it is colourless, crystalline, and melts at $74\text{--}75^{\circ}$. The *phenylhydrazone* crystallises in rhombic plates, melts at $149\text{--}150^{\circ}$, and is soluble in 7.8 parts of boiling alcohol. The yield is 80 per cent. of the theoretical. The ketone is converted by treatment with zinc and hydrochloric acid into *propyldihydrocoumarane*, $\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{O}\cdot\text{CHPr}^a$, a colourless, highly refractive liquid, with a pleasing odour; it boils at $254\text{--}257^{\circ}$ (760 mm.); the sp. gr. = 0.9946; it is insoluble in alkali, and gives a red color.

ation with sulphuric acid. The yield is 60 per cent. of the ketone employed.

Phenyl orthohydroxystyryl ketone (orthophenylcoumaroketone), $\text{HO}\cdot\text{C}_6\text{H}_4\cdot\text{CH}:\text{CH}\cdot\text{COPh}$, prepared from salicylaldehyde and acetophenone, is the sole product if soda (10 per cent.) is employed as the condensing agent (compare von Kostanecki and Bablich, this vol., i, 239); the yield is 70 per cent. of the aldehyde employed. The *phenylhydrazone* melts at 136° , and its solutions exhibit a blue fluorescence. The *tetrabromo*-derivative is readily prepared by the action of bromine in well-cooled glacial acetic acid solution; it crystallises in yellow needles, melts at $167\text{--}168^\circ$, and decomposes when boiled with alcohol. von Kostanecki and Bablich state (*loc. cit.*) that the ketone is decomposed by bromine. The *benzoyl*-derivative is crystalline, and melts at 102° .

Phenylorthohydroxybenzylcarbinol (phenyldihydrocoumaryl alcohol), $\text{HO}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CHPh}\cdot\text{OH}$, is formed when the above ketone is reduced by means of sodium amalgam; it crystallises in microscopic needles, melts at $96\text{--}97^\circ$, and gives a red coloration with concentrated sulphuric acid. The yield is 65 per cent. of the ketone. By the action of methylic alcoholic hydrochloric acid on the preceding compound,

dihydrophenylcoumarane, $\text{C}_6\text{H}_4\cdot\begin{matrix} \text{CH}_2\cdot\text{CH}_2 \\ | \\ \text{O}-\text{CHPh} \end{matrix}$, is formed; it is crystalline, melts at $44\text{--}45^\circ$, has a pleasing smell, does not dissolve in alkali, gives no coloration with sulphuric acid, and, at 18° , 1 gram dissolves in 7 c.c. of alcohol. The yield is 80 per cent. of the alcohol employed.

J. B. T.

Phenylchloriodopropionic acid and its Derivatives. By EMIL ERLÉNMEYER (*Annalen*, 1896, **289**, 259—284).—*Phenylchloriodopropionic acid*, $\text{CHPhCl}\cdot\text{CHI}\cdot\text{COOH}$, is formed when cinnamic acid is treated with an ethereal solution of iodine chloride containing hydrogen chloride; it crystallises in colourless leaflets, becomes red at 100° , and melts at $122\text{--}123^\circ$, yielding gas. Protracted treatment with cold water converts it into phenyliodolactic acid, which is produced immediately by boiling water; aqueous potassium iodide gives rise to cinnamic acid. The *methylic* salt separates from petroleum in colourless crystals, and melts at $97\text{--}98^\circ$, becoming red; the *ethylic* salt becomes red, and melts at $69\text{--}70^\circ$.

β-Ethoxyphenyl-α-iodopropionic acid, $\text{OEt}\cdot\text{CHPh}\cdot\text{CHI}\cdot\text{COOH}$, is obtained by the action of alcoholic potash on the foregoing acid; it crystallises from water in long needles containing $1\text{H}_2\text{O}$, and becomes red and melts at $138\text{--}139^\circ$.

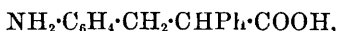
β-Methoxyphenyl-α-iodopropionic acid crystallises from water in anhydrous needles, and melts, becoming red at $164\text{--}165^\circ$.

Phenyliodohydracrylic acid, $\text{OH}\cdot\text{CHPh}\cdot\text{CHI}\cdot\text{COOH}$, is formed when sodium cinnamate is treated with an aqueous solution of iodine chloride containing hydrogen chloride; it crystallises from benzene in long, colourless prisms, and melts at $140\text{--}142^\circ$ when it becomes red, and evolves gas. The substance decomposes in aqueous solution when the latter is boiled for a protracted period, yielding iodine, phenylacetaldehyde, cinnamene, and cinnamic acid; reduction of phenyliodohydracrylic acid with sodium amalgam gives rise to phenyl-

hydracrylic acid. Boiling aqueous soda converts phenyliodohydracrylic acid into phenylglycidic acid, whilst hot hydrochloric acid gives rise to the compound, $C_{18}H_{16}ClIO_4$, which contains phenylchloriodopropionic acid and cinnamic acid in molecular proportion; it becomes red at 70° , and melts at $110-115^\circ$, when it decomposes. This substance yields cinnamic, hydrochloric, and phenyliodohydracrylic acids when treated with hot water, and phenylpropionic acid is formed on reduction with sodium amalgam, whilst potassium iodide gives rise to cinnamic acid. M. O. F.

New Synthesis of Phenanthrene and its Derivatives. By ROBERT PSCHORR (*Ber.*, 1896, **29**, 496—501).— α -Phenylorthonitrocinnamic acid, $NO_2 \cdot C_6H_4 \cdot CH : CPh \cdot COOH$, is obtained by heating ortho-nitrobenzaldehyde with sodium phenylacetate, acetic anhydride, and zinc chloride. It crystallises in colourless needles, and melts at $193-195^\circ$. α -Phenylorthamidocinnamic acid crystallises in narrow, yellow prisms, and melts at $185-186^\circ$. It dissolves in both acids and alkalis; the hydrochloride melts and decomposes at 218° , and the platinochloride melts at 220° . The acid also exists in a colourless modification, which is formed when it is recrystallised from water and passes into the yellow form at about 150° . Both forms of the acid are converted into β -phenanthrenecarboxylic acid, melting at $250-252^\circ$, when they are diazotised in sulphuric acid solution, and then treated with precipitated copper. The acid produced is identical with that previously described by Japp (*Trans.*, 1880, 84), and yields phenanthrene when distilled.

α -Phenylorthamido- β -phenylpropionic acid,



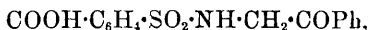
is formed by the action of sodium amalgam on amidophenylcinnamic acid. It cannot be obtained in the free state, as when the alkaline solution is acidified, β -phenyldihydrocarbostyryl, $C_6H_4 \cdot \begin{smallmatrix} CH_2 \cdot CHPh \\ N = C(OH) \end{smallmatrix}$, which melts at 169° , is formed.

When the alkaline solution is treated with sodium nitrite and sulphuric acid, and then with precipitated copper, a syrupy acid is produced, which yields phenanthraquinone when treated with chromic anhydride and acetic acid. A. H.

α -Benzoylcoumarone. By E. RAP (*Gazzetta*, 1895, **25**, ii, 285—289).—On adding bromacetophenone to a hot, alcoholic potash solution of salicylaldehyde and concentrating the solution, an α -benzoylcoumarone, $C_6H_4 \cdot \begin{smallmatrix} CH \\ -O- \end{smallmatrix} > C \cdot CPh$, is obtained. This crystallises in long needles melting at $90-91^\circ$, and is very soluble in most organic solvents. It yields a hydrazone, $C_{15}H_{10}O : N_2HPh$, which crystallises in minute yellow needles, melting at $128-129^\circ$, and an oxime, $C_{15}H_{10}O : NOH$, melting at $125-128^\circ$; a substance melting at $126-135^\circ$, is also formed by the action of hydroxylamine.

W. J. P.

Action of Some Halogen Compounds containing Oxygen on Sodium Benzoicsulphinide (Saccharin). By HUGO ECKENROTH and KARL KLEIN (*Ber.*, 1896, **29**, 329—332).—The sodium derivative of benzoicsulphinide, $C_6H_4\langle\begin{smallmatrix} CO \\ SO_2 \end{smallmatrix}\rangle NNa$, reacts with various halogen compounds (compare Fahlberg and List, *Abstr.*, 1887, 835; *Ber.*, **20**, 1596). With monochloroacetone, $CH_3Cl\cdot CMeO$, at 100° , it yields *acetonylorthobenzoicsulphinide*, $C_6H_4\langle\begin{smallmatrix} CO \\ SO_2 \end{smallmatrix}\rangle N\cdot CH_2\cdot CMeO$, which melts at 143° , yields a yellow *phenylhydrazone*, melting at 166° , and a *monobromo-derivative*, melting at 168° , and is hydrolysed to orthosulphobenzoic acid, ammonia, and acetonalcohol. With bromoacetophenone, $CH_3Br\cdot COPh$, it reacts at 150° , in a similar way; the product, *phenacylorthobenzoicsulphinide*, melts at $194\cdot5^\circ$, yields a yellow *phenylhydrazone*, melting at 168° , and is hydrolysed by alcoholic potash to *phenacylsulphamidobenzoic acid*,



which melts at 160° .

C. F. B.

Diphenylselenone, SeO_2Ph_2 . By FRIEDRICH KRAFFT and ROBERT E. LYONS (*Ber.*, 1896, **29**, 424—428).—Diphenylselenoxide (*Abstr.*, 1894, 89), $OSePh_2$, is oxidised when it is boiled with aqueous permanganate, to *diphenylselenone*, which melts at 155° , and boils, with slight decomposition, at 270 — 271° under 9·5 mm. pressure. This substance loses oxygen when strongly heated, and phenylic selenide is formed. When it is heated with sulphur to 190° , a sudden reaction occurs, phenylic diselenide being formed, and sulphurous anhydride evolved. When it is boiled with strong hydrochloric acid, diphenylselenochloride, Cl_2SePh_2 , is formed, and chlorine is given off. It also liberates iodine from a solution of potassium iodide. The reactions of diphenylselenone are, in many points, analogous to those of iodoxybenzene, as are those of diphenylselenoxide to those of iodosobenzene.

Nitric acid oxidises phenylic diselenide to *phenylselenious acid*, the *nitrate* of which, $Ph\cdot SeO_2H\cdot HNO_3$ [$? SePh(OH)_2\cdot NO_3$], is a well crystallised substance; the hydrochloride of the corresponding ethylic compound was prepared long ago by Rathke (*Annalen*, **152**, 219). The substance in question has thus basic properties; it also has acid properties, and forms a well defined silver salt.

C. F. B.

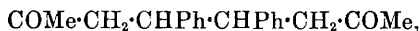
Carbazole Derivatives. By M. LAMBERTI-ZANARDI (*Gazzetta*, 1895, **25**, ii, 359—364).—*Benzoylchlorobromocarbazole*, $C_{12}H_6ClBrNBz$, is prepared by the action of chlorine on Mazzara and Leonardi's benzoylbromocarbazole (*Abstr.*, 1893, i, 349) in acetic acid solution. It crystallises in colourless needles melting at 202° , and is hydrolysed by boiling potash, giving *chlorobromocarbazole*, $C_{12}H_6ClBrNH$, which crystallises in iridescent scales melting at 197 — 198° ; when heated with acetic anhydride in a closed tube at 240° , it yields *acetylchlorobromocarbazole*, $C_{12}H_6ClBrNAc$, which crystallises in lustrous, colourless needles melting at 178 — 179° .

α -Benzoyldichlorodibromocarbazole, $C_{19}H_9NOCl_2Br_2$, obtained by direct chlorination of benzoyldibromocarbazole in presence of iodine, crystallises in opaque, white needles melting at $267-268^\circ$; it is accompanied by a β -isomeride, which crystallises in small, opaque, white prisms melting at $238-240^\circ$, and by another substance melting at $190-215^\circ$, which could not be purified. W. J. P.

γ -Carbodiphenylimide. By J. F. CARL SCHALL (*J. pr. Chem.*, 1896, [2], 53, 139-142).—The author reviews the criticisms which Miller and Plöchl (*Abstr.*, 1895, i, 415) have passed on his work on the carbodiphenylimides, and claims that the γ -derivative, whether freshly prepared or after long standing, contains at least one physical modification of β -carbodiphenylimide. A. G. B.

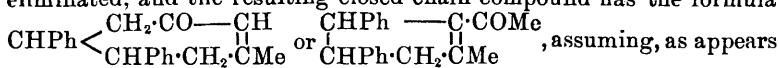
The Diphenylhydroxyethylamine Bases. By EMIL ERLMEYER, jun. (*Ber.*, 1896, 29, 295-298).—The reduction of benzoïnoxime yields a phenylhydroxyethylamine which melts at 161° , along with a second substance melting at $129-130^\circ$ (Söderbaum, this vol., i, 98), which can be resolved by crystallisation into two isomeric substances, one of which crystallises in thin prisms or three-sided, pointed needles belonging to the hexagonal system, whilst the other crystallises in rectangular tablets. The same two compounds, melting at $129-130^\circ$, are also formed, but in different proportions, by the condensation of benzaldehyde with glycocine (*Abstr.*, 1895, i, 596). Three isomerides of phenylhydroxyethylamine have, therefore, been described, and the relations in which they stand to one another have not yet been ascertained. The isomeride melting at 161° is converted, by means of the diazo-reaction, into isohydrobenzoïn, and not into hydrobenzoïn. A base, melting at 128° , has also been observed by Polonowska among the products of the reduction of benzilmonoxime (*Abstr.*, 1888, 485). A. H.

Reduction of Unsaturated Ketones. By CARL D. HARRIES and G. ESCHENBACH (*Ber.*, 1896, 29, 380-388).—Engler and Leist, who discovered benzylideneacetone, state that it is converted into a secondary alcohol when reduced by means of sodium amalgam in dilute alcoholic solution, but the authors only obtained resinous products under these conditions; if the liquid is well cooled and maintained acid by the addition of dilute acetic acid, benzylacetone and diphenyl-4 : 5-octanedione-2 : 7,



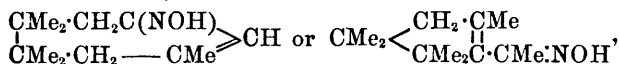
is formed; it crystallises in long, colourless, transparent, triclinic parallelopipeds, melts at 161° , boils at $335-340^\circ$ under the ordinary pressure, and at $221-222^\circ$ (10 mm.). It is not volatile with steam, does not combine with sodium hydrogen sulphite, and dissolves in concentrated sulphuric acid with a green coloration. The yield is about 10 per cent. of the diketone and 30 per cent. of benzylacetone; but if aluminium amalgam is employed, the yield of diketone is improved, and benzylacetone is only formed in very small quantity. Attempts to obtain a pyrroline or pyridine derivative were unsuccessful, as, when reduced with sodium and boiling alcohol, or with sodium amalgam in alkaline

solution, amorphous compounds are formed; in acid solution, the diketone is not changed; with zinc dust and alcoholic hydrochloric acid, a compound is obtained which melts at 120°, and has not been investigated. The diketone is not oxidised by sodium hypochlorite, potassium dichromate and sulphuric acid, or acetic acid; with chromic anhydride and glacial acetic acid, benzoic acid is formed. With concentrated nitric acid, two yellow, nitrogenous products are obtained, the one by gently heating, the other when the acid is boiled; they melt at about 130° and 67—68° respectively. The *diphenylhydrazone* is sparingly soluble, darkens at 170°, melts at 194°, and could not be recrystallised. The *dioxime* softens at 200°, and melts at 235—237°. No monoxime or monophenylhydrazone could be obtained. By the action of sodium ethoxide on the above diketone, water is eliminated, and the resulting closed chain compound has the formula

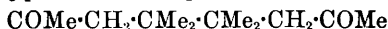


probable, that the diketone has the formula assigned to it; it crystallises in transparent plates, melts at 87°, boils at 214—215° (8.5 mm.), and at about 330—335° under the ordinary pressure. It is not volatile with steam, and resembles the diketone in its action towards oxidising agents. The yield is 70—80 per cent. of the theoretical. Attempts to reduce the compound by means of sodium in alcoholic solution have not yielded any definite results, and no crystalline oxime or phenylhydrazone has hitherto been obtained.

Mesityl oxide resembles benzylideneacetone in its action towards reducing agents; the product obtained by the action of aluminium amalgam was fractionated, and the portion boiling at 210—220° converted into the *oxime*,



which crystallises with 1H₂O in long, broad prisms, melts at 156—157°, has a camphor-like odour, readily volatilises at the ordinary temperature, and, in small quantity, may be distilled without decomposition; it does not reduce Fehling's solution, and, when heated with concentrated hydrochloric acid, the ketone is regenerated. The reduction product of mesityl oxide differs from that of benzylideneacetone in stability, the hypothetical compound,



which is first formed condensing spontaneously to the above closed chain derivative. J. B. T.

Synthesis of Pararosaniline and its Mono-, Di-, Tri-, and Tetra-alkylic Derivatives. By MAURICE PRUD'HOMME (*Compt. rend.*, 1895, 121, 891—893).—When the paranitrodiamidotriphenylmethanes are dissolved in hydrochloric acid and treated with zinc dust at the ordinary temperature, they yield complex hydroxylamines [$\text{CH} \cdot \text{C}_6\text{H}_4 \cdot \text{NR}_2 : \text{NH} \cdot \text{OH} = 1 : 4$], and when the latter are heated with hydrochloric acid they yield coloured products, the hydroxylamine group being changed into the amido-group, just as phenylhydroxyl-

amine is converted into paramidophenol, and this notwithstanding the fact that it is the central carbon which occupies the para-position with respect to the hydroxylamine. The products have, therefore, the constitution $[\text{C}(\text{OH})\cdot\text{C}_6\text{H}_4\cdot\text{NR}_2:\text{NH}_2 = 1:4]$. The intermediate leuco-bases are precipitated by adding sodium acetate, and, after the zinc has been removed from the liquid, the colouring matters can be separated by means of alcohol.

To obtain paranitro-compounds corresponding with pararosanine and its derivatives, 1 mol. of paranitrobenzaldehyde is condensed directly with 2 mols. of aniline or dialkylanilines. The mono- and tri-alkyl-derivatives are obtained by condensing monalkylparanitro-amidohydroxydiphenyl with aniline or dialkylanilines. Similarly, the dialkylrosanilines may contain alcohol radicles in one or two nuclei.

The colour of these derivatives becomes more violet as the number of alkylic radicles in the amido-groups increases, the substitutions having more effect in this respect if they take place in the same nucleus than if they take place in two different benzene nuclei.

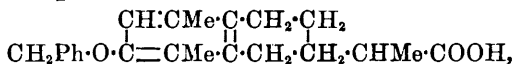
C. H. B.

Desmotroposantonin and the Benzylsantonous acids. By NICOLA CASTORO (*Gazzetta*, 1895, 25, ii, 348—359).—Benzyl-desmotroposantonin, $\text{CH}_2\text{Ph}\cdot\text{O}\cdot\text{C}\equiv\text{CMe}\cdot\text{C}\cdot\text{CH}_2\cdot\text{CH}\cdot\text{CHMe}$ $\xrightarrow{\text{O}} \text{CO}$, is obtained

by allowing an alcoholic solution of sodium ethoxide containing desmotroposantonin and benzylic chloride to remain for some days; it crystallises in white needles melting at $181\text{--}182^\circ$, and is soluble in ether. Its specific rotation is $[\alpha]_D = +102.6^\circ$, and it is readily hydrolysed by boiling with potash, yielding potassium benzyldesmotroposantonate.

The isomeric *benzyldesmotroposantonin*, prepared in a similar manner from isodesmotroposantonin, crystallises in transparent needles melting at $81\text{--}82^\circ$, has the specific rotation $[\alpha]_D = +136.5^\circ$, and is very soluble in ether. It is hydrolysed by boiling potash, giving a salt of benzylisodesmotroposantononic acid.

Benzyldesmotroposantonous acid,

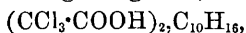


is prepared by reducing benzyldesmotroposantonin with zinc dust and acetic acid; it crystallises in transparent needles melting at $121\text{--}123^\circ$, and has the specific rotation $[\alpha]_D = -39.3^\circ$. The sodium salt crystallises in lustrous laminæ. W. J. P.

The Anhydride and Decomposition Products of Ethylic Santonite. By NICCOLÒ RIZZO (*Gazzetta*, 1895, 25, ii, 290—298).—On distilling ethylic dextrosantonite at $360\text{--}370^\circ$, hydrogen is evolved, and after treating the distillate with water, the aqueous liquid is found to contain ethylic alcohol and propionic acid; in the oily part of the distillate, ethylic propionate, dimethyldihydronaphthol, and the *anhydride*, $\text{C}_{31}\text{H}_{42}\text{O}_5$, of ethylic dehydrosantonite were found. W. J. P.

Conversion of Bromoprotocatechuic acid into a Dibromorthonaphthaquinonecarboxylic acid. By THEODOR ZINCKE (*J. pr. Chem.*, 1896, [2], 53, 100—105).—Oxidation of bromoprotocatechuic acid by dilute nitric acid yields a compound of the formula $C_{11}H_4Br_2O_4$, which is probably 3:1'-dibromo-1:2-naphthaquinone-3'-carboxylic acid, but it remains uncertain whether 3:4':1:2:2' be not the correct orientation. Much oxalic acid is formed during the oxidation. Towards an alkali, the new compound behaves in part like a bromo- β -naphthaquinone, and in part like a diketone; the first reaction leads to the formation of a hydroxyparaquinone, the second to that of a dibasic acid, $C_{11}H_6Br_2O_6$. Formulæ showing the probable orientation of these compounds, and of those produced by treating them with bleaching powder, are given in the paper. A. G. B.

Action of Trichloroacetic acid on Terpenes. By ALBERT REYCHLER (*Ber.*, 1896, 29, 695—697).—When carvene and trichloroacetic acid (2 mols.) are brought together, the compound,



is formed; it is optically inactive, crystallises in lustrous leaflets melting at 104° , and yields terpin hydrate when hydrolysed.

Pinene gives rise to borneol when the hydrocarbon is in excess, but in presence of excess of trichloroacetic acid, the foregoing compound is produced.

Camphene is converted into a salt of isoborneol. M. O. F.

Orientation in the Terpene Series. By ADOLF VON BAEYER (*Ber.*, 1896, 29, 326—329; compare this vol., i, 245).— α -Pinonic acid (*loc. cit.*) is readily obtained by the oxidation of pinene at 30° , it being unnecessary to fractionate the product. If an acid solution is employed at the ordinary temperatures, small quantities of the hydrocarbon may be converted into the crystalline acid in five minutes.

When α -pinonic acid is heated for 30 minutes on the water bath with 10 parts of 50 per cent. sulphuric acid, it is converted into the isomeric lactone (m. p. 63 — 65°), identical with the substance obtained by Wallach on oxidising terpineol, and by Tiemann and Semmler from the oxidation products of pinene (*Abstr.*, 1895, i, 548). The author expresses the constitution of α -pinonic acid by the formula

$COOH \cdot CH_2 \cdot CH < \begin{smallmatrix} CMe_2 \\ CH_2 \end{smallmatrix} > CH \cdot COMe$, the isomeric lactone having the structure $\begin{smallmatrix} O & \text{---} & CMe_2 \\ | & & | \\ CO \cdot CH_2 & \cdot & CH \cdot CH_2 \cdot CH_2 \cdot COMe \end{smallmatrix}$. Oxidation of α -pinonic acid

with dilute nitric acid gives rise to pinic, oxalic, and terebic acids.

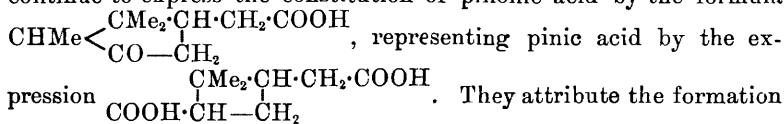
Hydroxy-pinic acid, $C_9H_{14}O_5$, is obtained by treating pinic acid with phosphorus pentachloride and bromine, converting the bromo-acid thus formed into the acetyl derivative by the action of silver acetate, and hydrolysing the acetyl derivative. It crystallises from water in prisms, and melts at 193 — 194° . M. O. F.

Pinonic acid. By FERDINAND TIEMANN and FRIEDRICH W. SEMMLER (*Ber.*, 1896, 29, 529—544; compare *Abstr.*, 1895, i, 477, and von Baeyer, this vol., i, 246).—The result of oxidising pinene with potassium permanganate is entirely controlled by conditions of tempera-

ture, liquid pinonic acid being formed at 6° , whilst von Baeyer's α -pinonic acid is the sole product when the temperature is maintained at $25-40^{\circ}$; the solid acid, however, slowly induces crystallisation in the liquid modification, which thus yields one-half its weight of α -pinonic acid. One decimetre of freshly distilled liquid pinonic acid has $\alpha = +6^{\circ}$, this rotation being increased to $\alpha = +13^{\circ}$ when the solid acid has been removed; the latter has $\alpha = +2^{\circ}$ in a tube of the same length, whilst *l*-pinonic acid, obtained by distilling α -dihydroxydihydrocampholenic acid, has $\alpha = -21^{\circ}$. The *semicarbazone* of *l*-pinonic acid melts at 231° , and the *oxime* at 125° , or at 131° after successive recrystallisations from water; the *semicarbazone* of *d*-pinonic acid melts at 207° , and the *semicarbazone* of α -pinonic acid melts between 197° and 211° . The formation of methoethylheptanonolide (m. p. $63-65^{\circ}$), which von Baeyer obtained from α -pinonic acid (*loc. cit.*), is observed when all the modifications of pinonic acid are treated with acids, and also occurs when they are distilled slowly under atmospheric pressure.

The formation of optically active pinonic acids from active pinenes would seem to indicate that the oxidation process is a simple one, and the authors have shown that the change in question is not dependent on the intermediate formation of α -dihydroxydihydrocampholenic acid; it is probable that *d*- and α -pinonic acids are different configurations of the same substance, and this view is supported by the production of isoketocamphoric and isocamphoric acids when both acids are oxidised.

The authors have stated that *d*-pinonic acid is indifferent towards alkali hypobromite (Abstr., 1895, i, 478); action does occur slowly, however, and the *l*-acid is also decomposed. The production of bromoform does not necessarily imply the presence of the group $\cdot\text{CO}\cdot\text{CH}_2$, because the behaviour of *iretol* (Abstr., 1894, i, 49) and *tanacetone* (Abstr., 1893, i, 107) has shown otherwise; the authors, therefore, continue to express the constitution of pinonic acid by the formula

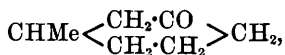


They attribute the formation of pinic acid, on oxidation of pinonic acid with nitric acid, to preliminary molecular rearrangement, and ascribe the conversion of pinonic acid into methoethylheptanonolide to the same cause. This change is illustrated by the transformation of *tanacetoketocarboxylic acid* into methoethylheptanonolide, and the production of an analogous lactonic acid from *tanacetogendicarboxylic acid*. M. O. F.

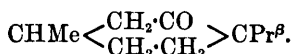
Terpenes and Ethereal Oils. Pulegone. By OTTO WALLACH (*Annalen*, 1896, 289, 337—361; compare Abstr., 1893, i, 115).—When *pulegone* is heated with its own volume of anhydrous formic acid in a reflux apparatus, or with water at 250° , acetone is produced along with a *methylcyclohexenone*, $\text{C}_7\text{H}_{12}\text{O}$, which boils at 169° , has the sp. gr. = 0.915 at 21° , and the refractive index $n_D = 1.4456$ at the same temperature, whence the molecular refraction $M = 32.59$;

the *semicarbazone* melts at 180° , and the *oxime* at $43\text{--}44^{\circ}$. The *cycloheptenamine*, $\text{C}_7\text{H}_{13}\cdot\text{NH}_2$, obtained by heating pulegone with ammonium formate (*loc. cit.*), is also produced when the foregoing oxime is reduced in alcoholic solution with sodium; it boils at 151° , and the *carbamide* and *semicarbazone* melt at 178° and 177° respectively. The formation of this primary base is attended with the production of a secondary base, $\text{NH}(\text{C}_7\text{H}_{13})_2$, which boils at 273° , and crystallises in needles (Abstr., 1894, i, 154); the *nitrate* is not very soluble.

Reduction of the foregoing methylhexenone with sodium and alcohol gives rise to *methylcyclohexenol* (*metahydroxyhexahydrotoluene*), $\text{C}_7\text{H}_{13}\cdot\text{OH}$, which boils at 77° under a pressure of 17 mm., and at $175\text{--}176^{\circ}$ under atmospheric pressure; the sp. gr. = 0.914 at 19° , and the refractive index $n_D = 1.4581$ at the same temperature, whence the molecular refraction $M = 34.04$. The *iodide*, $\text{C}_7\text{H}_{13}\text{I}$, is obtained from the alcohol by means of iodine and amorphous phosphorus; it boils at $100\text{--}110^{\circ}$ under a pressure of 30 mm., and is converted by quinoline into tetrahydrotoluene, which has been isolated from resin oil by Renard. When the methylcyclohexenone is oxidised with potassium permanganate, it yields an acid, which melts at 69° , and closely resembles the pimelic acid obtained from menthone, which, however, melts at $84\text{--}85^{\circ}$. In view of the foregoing observations, the author expresses the constitution of this ketone by the formula



and advocates Semmler's formula for pulegone,



The methylcyclohexenone is isomeric with Markownikoff's suberone (Abstr., 1894, i, 160), which yields the *semicarbazone*, melting at $163\text{--}164^{\circ}$.

Pulegoneamine (Abstr., 1895, i, 153) boils at $205\text{--}210^{\circ}$; the *carbamide* is obtained from the *hydrochloride*, and melts at $104\text{--}105^{\circ}$, and the *phenylcarbamide* crystallises from alcohol, and melts at $154\text{--}155^{\circ}$.

Pulegenic acid, $\text{C}_{10}\text{H}_{16}\text{O}_2$, is obtained by heating a solution of pulegone dibromide in methylic alcohol with sodium for four hours; it undergoes decomposition when boiled at atmospheric pressure, but boils at 155° under a pressure of 13 mm. The sp. gr. = 1.007 at 19° , and the refractive index $n_D = 1.48071$ at the same temperature. The *ammonium* salt is white, and the *amide* crystallises in woolly needles, and melts at $121\text{--}122^{\circ}$; the *nitrile* boils at $218\text{--}220^{\circ}$, has the sp. gr. = 0.8935 at 22° , and the refractive index $n_D = 1.47047$ at the same temperature. Reduction of the nitrile converts it into a *base*, having the odour of menthylamine; the *carbamide* melts at $97\text{--}99^{\circ}$. The *hydrochloride* of methylic pulegenate boils at $113\text{--}116^{\circ}$ under a pressure of 12 mm., and solidifies at low temperatures.

The *hydrocarbon*, C_9H_{16} , is produced when pulegenic acid is dis-

tilled under atmospheric pressure; it boils at 138—140°, has the sp. gr. = 0.79 at 20°, and the refractive index $n_D = 1.44$ at the same temperature, whence the molecular refraction $M = 41.37$. The *nitrosochloride* melts at 74—75°.

The *hydroxylactone*, $C_{10}H_{16}O_3$, obtained by oxidising pulegenic acid with potassium permanganate, melts at 129—130°, and boils at 185° under a pressure of 20 mm.; it is also produced by the action of chromic acid. The *ketone*, $C_9H_{16}O$, is formed when the hydroxylactone is treated with sulphuric acid, carbonic anhydride being eliminated; it boils at 183°, and has the sp. gr. 0.8925 at 21°, and the refractive index $n_D = 1.44506$ at the same temperature. The *carbazone* and *oxime* melt at 169—170° and 94° respectively.

The author compares pulegenic acid with campholenic and fencholenic acids, and develops formulæ for the compounds just described.

M. O. F.

Oil of Lemon-grass. By PHILIPPE BARBIER and LOUIS BOUVEAULT (*Compt. rend.*, 1895, **121**, 1159—1162).—That portion of the oil of lemon-grass which boils at 107—110° under a pressure of 10 mm. yields a semicarbazone, $C_{11}H_{19}N_3O$, which forms white lamellæ, melting at 171°, and is very slightly soluble in boiling alcohol. That portion of the oil which boils at 110—112° under a pressure of 10 mm. yields three isomeric semicarbazones of the composition



One forms white lamellæ, melting at 171°, and is identical with that obtained from the lower fraction; another crystallises in needles, melts at 160°, and is very soluble in hot alcohol, but only moderately so at the ordinary temperature; and a third forms white needles, which melt at 135°, and are very soluble in cold alcohol.

When the semicarbazone melting at 171°, is boiled with dilute sulphuric acid, it yields paracymene and an aldehyde, which, with semicarbazide, forms the semicarbazone melting at 135°. Under similar conditions, the semicarbazone melting at 135°, yields cymene, and an aldehyde which can be reconverted into the original semicarbazone.

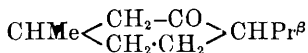
These results are not caused by any stereoisomerism due to nitrogen, and it would seem that oil of lemon-grass contains two acyclic aldehydes, one of which, $CH_2\cdot CMe\cdot CH(COH)\cdot CH_2\cdot CH\cdot CMe_2$, is converted into the other, $CMe_2\cdot C(COH)\cdot CH_2\cdot CH\cdot CMe_2$, by the action of dilute sulphuric acid.

The oil of lemon-grass does not contain an aldehyde of the composition $C_{10}H_{18}O$ (compare Abstr., 1894, i, 400—401).

C. H. B.

The Camphor Series III: Menthones. By ERNST BECKMANN (*Annalen*, 1896, **289**, 362—367; compare Abstr., 1889, 722, and 1894, i, 240).—The author has observed that acids and bases exercise an inverting influence on lævo-menthone, transforming it into a dextrorotatory modification (*loc. cit.*); concentrated sulphuric acid, for example, gives rise to a product which is dextrorotatory in the same degree as the original material is lævogryate. The oxime of the latter, however, has the specific rotatory power $[\alpha]_D = -40.75^\circ$.

to -41.97° , whilst the oxime from the dextrorotatory menthone has the specific rotatory power $[\alpha]_D = -4.85^\circ$ to -6.67° ; it is found, moreover, that as the dextrogyrate character of the menthone becomes intensified, hydroxylamine gives rise to a preponderating amount of the liquid oxime, until finally the product does not yield crystals. The author endeavours to explain the mechanism of this change, basing his considerations on the formula

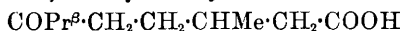


for menthone.

Lævo-menthone *semicarbazone* crystallises from alcohol in small needles, melts at 178° , and has the specific rotatory power $[\alpha]_D = -3.67^\circ$ in glacial acetic acid (10 per cent. solution) at 20° ; the *semicarbazone* of dextro-menthone has $[\alpha]_D = -3^\circ$ under the same conditions, and melts at 172° , a mixture of the two isomerides melting at 175° .

M. O. F.

Menthones. By ERNST BECKMANN and H. MEHRLÄNDER (*Annalen*, 1896, **289**, 367—391).—Oxymenthylic acid,



(compare Manasse and Rupe, *Abstr.*, 1894, i, 470), is obtained by oxidising menthone with chromic anhydride, and boils at 292° ; it is also produced when menthol is oxidised with potassium permanganate, and was obtained in this way by Arth (*Abstr.*, 1886, 892).

Menthoximic acid, $\text{C}_{10}\text{H}_{18}\text{O}_2 \cdot \text{NOH}$, obtained by von Baeyer and Manasse from menthone under the influence of amylic nitrite (*Abstr.*, 1894, i, 522), is produced by the action of hydroxylamine on the foregoing acid; the *sodium* salt is deliquescent, and the *copper* and *silver* salts are amorphous. The *ethylic* salt is a colourless oil, and the *acetyl* derivative is crystalline, and melts at 91° .

Bromine converts oxymenthylic acid into an oil, which probably has the formula $\text{C}_{10}\text{H}_{16}\text{O}_3\text{Br}_2$. The action of bromine on lævo-menthone converts it into a *compound*, $\text{C}_{10}\text{H}_{17}\text{Br}_3\text{O}$, a brown oil, which fumes in moist air, and has a disagreeable odour.

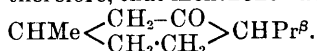
The conversion of *l*-menthoneoxime into an isomeride under the influence of phosphorus pentachloride has been observed by Wallach (*Abstr.*, 1894, i, 46 and 337). The same agent acting on *d*-menthoneoxime gives rise to an isomeric *compound*, which crystallises from water, and melts at 88° ; a solution in 4 parts of alcohol has the rotatory power $\alpha = -4.9^\circ$ in a 1 decimetre tube at 20° , and the liquid *hydrochloride*, under the same conditions, has the rotatory power $\alpha = -3.67^\circ$. An oily, isomeric *compound* is formed along with the solid substance, and, under the above mentioned conditions, has the rotatory power $\alpha = -1.87^\circ$.

Concentrated sulphuric acid at 100° converts *l*-menthoneoxime into an isomeric *compound*, which melts between 68° and 83° , and although this product appears to consist of a mixture of two substances, attempts to resolve it into constituents have been unsuccessful; it is indifferent towards organic bases, benzoic chloride, phenylcarbamide, sodium amalgam, hydriodic acid, and zinc dust, but yields a hydro-

chloride, which melts at 91°. Phosphorus pentachloride gives rise to an oil, which, when treated with aqueous soda, yields the compound (m. p. 120°) obtained by the action of phosphorus pentachloride on *l*-menthoneoxime (Abstr., 1894, i, 46). M. O. F.

The Menthones; Conversion into Thymol. By ERNST BECKMANN and H. EICKELBERG (*Ber.*, 1896, **29**, 418—421).—*Dibromomenthone*, $C_{10}H_{16}Br_2O$, is obtained by adding bromine (2 mols.) to *l*- or *d*-menthone dissolved in four parts by weight of chloroform, and, after adding ether and agitating with soda, allowing the reddish-brown oil obtained on evaporation to lose hydrogen bromide spontaneously; it separates from alcohol in colourless crystals, and melts at 79—80°. A 3.05 per cent. solution in carbon tetrachloride has the specific rotatory power $[\alpha]_D = +199.4^\circ$. Zinc dust is without action on dibromomenthone in alcoholic solution, but in presence of glacial acetic acid, menthone is regenerated; hydroxylamine converts it into the *oximido*-compound, $OH \cdot C_{10}H_{16}Br \cdot NOH$, which crystallises from light petroleum, and melts at 136—137°.

When dibromomenthone is heated for five minutes with boiling quinoline (6 mols.), thymol is produced, and the authors conclude, therefore, that menthone has the constitution expressed by the formula



M. O. F.

Halogen Derivatives of Camphene and Hydrocamphene.

By ERNST JÜNGER and A. KLAGES (*Ber.*, 1896, **29**, 544—547).—When camphene hydrochloride is treated with glacial acetic acid, isobornylic acetate is formed; the fact that bornylic chloride yields the same product, is probably owing to initial regeneration of camphene (compare Bertram and Walbaum, Abstr., 1894, i, 204).

Camphene hydrochloride, which melts at 165°, unites with bromine forming an oil which yields bromocamphene when distilled with quinoline; this substance, which has been described by Wallach (*Annalen*, **230**, 293), boils at 226—227°, has the sp. gr. = 1.265 at 15°, the refractive index $n_D = 1.52605$ at 15°, and the molecular refraction $M = 52.36$.

From the similarity exhibited by isobornylic chloride and bornylic chloride, the authors regard isoborneol and its derivatives as geometrically isomeric with the corresponding borneol derivatives.

M. O. F.

Isobornylic Chloride and Camphene Hydrochloride. By ALBERT REYCHLER (*Ber.*, 1896, **29**, 697—699).—Both camphene and isoborneol yield isobornylic chloride when hydrogen chloride is led into the alcoholic solution; although indifferent towards alcoholic hydrogen chloride, phosphorus pentachloride converts borneol into bornylic chloride, and the author, therefore, regards isobornylic chloride and camphene hydrochloride as identical, and stereoisomeric with bornylic chloride.

M. O. F.

Derivatives of Camphoric and Hemipinic acids. By SEBASTIAAN HOOGEWERFF and WILLEM A. VAN DORP (*Rec. Trav. Chim.*, 1895,

14, 252—275).—The authors have prepared α -camphoramic acid by a method differing but slightly from that recommended by Auwers and Schnell (Abstr., 1893, i, 525). It is best purified by conversion into its hydrochloride by passing dry hydrogen chloride into an alcoholic solution of the acid; the pure hydrochloride is then decomposed by treatment with water. It crystallises in colourless plates, melts at 176—177°, and is fairly soluble in hot water, readily in acetone and alcohol, sparingly in ether, chloroform, and benzene. Its rotatory power in alcoholic solution is $[\alpha]_D = +45^\circ$. Nitrous acid converts it into camphoric acid. The *silver* salt forms colourless crystals; the *copper* salt crystallises with 4H₂O in small spheres.

α -Camphorisoimide hydrochloride, $C_8H_{14} < \begin{smallmatrix} C(NH) \\ CO \end{smallmatrix} > O, HCl$, is obtained when the α -camphoramic acid is heated with about four times its weight of acetic chloride (compare Abstr., 1893, i, 599). It is somewhat unstable, and is rapidly transformed by water into α -camphoramic acid. It forms an *aurochloride*, $C_9H_{15}NO_2 \cdot AuCl_4$, which is a yellow, crystalline compound, and melts at 120—130°. When the hydrochloride is decomposed with potassium or ammonium hydroxide, it is converted into a salt of *cyanolauronic acid*, $CN \cdot C_8H_{14} \cdot COOH$. This acid crystallises in orthorhombic prisms, and melts at 151—152° without undergoing decomposition. When rapidly distilled, it passes over unaltered, but if kept at the boiling point for some time it is transformed into camphorimide, $C_8H_{14} < \begin{smallmatrix} CO \\ CO \end{smallmatrix} > NH$, and when boiled with concentrated hydrochloric acid it is hydrolysed to camphoric acid. Its alcoholic solution is optically active, $[\alpha]_D = +67^\circ 30'$. Its *silver* salt is only slightly sensitive to light. The *methylic* salt melts at 40—42°, and the *ethylic* salt at 24—27°. Cyanolauronic acid, when reduced with sodium and alcohol, yields the acid $NH_2 \cdot CH_2 \cdot C_8H_{14} \cdot COOH$, the *platinochloride* of which forms yellowish plates, and does not melt below 270°.

β -Camphoramic acid is obtained, together with a small quantity of the isomeric α -acid, on treating camphorimide with sodium hydroxide (compare Noyes, Abstr., 1894, i, 339). It crystallises in prisms or plates, melts at 180—181° (Noyes 182—183°), is readily soluble in alcohol, acetone, and hot water, sparingly in ether, benzene, and chloroform; its alcoholic solution has a rotatory power $[\alpha]_D = +60^\circ$. When treated with nitrous acid, it yields ordinary dextro-camphoric acid.

β -Camphorisoimide hydrochloride is obtained when the above acid is heated with acetic chloride, and yields a yellow, crystalline *aurochloride*. On treating the hydrochloride with aqueous ammonia and then acidifying, *cyanodihydrocampholytic acid*, $CN \cdot C_8H_{14} \cdot COOH$, is formed; this acid crystallises in monoclinic plates, melts at 109—111°, and has a rotatory power $[\alpha]_D = +18^\circ 12'$.

Methyl- β -camphoramic acid, $NHMe \cdot CO \cdot C_8H_{14} \cdot COOH$, is obtained on treating camphormethylimide (compare Abstr., 1893, i, 599) with sodium hydroxide. It crystallises with 1H₂O in oblong plates, loses its water at 80°, and then melts at 177—178°; it is readily soluble

in alcohol and acetone, sparingly in benzene, and still more sparingly in ether.

β -Camphormethylisoimide, obtained by the action of phosphorus oxychloride on methyl- β -camphoramic acid, crystallises in colourless needles, melts at $85-86.5^\circ$, and boils at $255-258^\circ$ (uncorr.) with only slight decomposition; it dissolves in dilute hydrochloric acid, but is quickly hydrolysed to the methylamic acid. It yields a *hydrochloride* and also an *aurochloride*.

α -Hemipinamic acid, $\text{NH}_2 \cdot \text{CO} \cdot \text{C}_6\text{H}_2(\text{OMe})_2 \cdot \text{COOH}$ [= 2 : 3 : 4 : 1], is formed, together with a small quantity of the isomeric β -acid, when hemipinic anhydride is dissolved in aqueous ammonia and then acidified with a mineral acid. It crystallises in colourless needles with $2\text{H}_2\text{O}$, which it loses at 80° , and then melts at $160-162^\circ$, at the same time undergoing decomposition and yielding hemipinimide, which melts at 220° . The acid is moderately soluble in alcohol, sparingly in acetone, and very sparingly in benzene and ether. Hot water dissolves it, but at the same time converts it into the imide. The *silver* salt of the α -acid is a colourless, crystalline precipitate.

Cyanodimethoxybenzoic acid, $\text{CN} \cdot \text{C}_6\text{H}_2(\text{OMe})_2 \cdot \text{COOH}$ [= 2 : 3 : 4 : 1], is obtained from the α -acid in exactly the same way as cyanolauronic acid from α -camphoramic acid. It crystallises in colourless needles, melts at $207-208^\circ$, and is readily converted into the α -hemipinamic acid on exposure to moist air.

β -Hemipinamic acid, $\text{NH}_2 \cdot \text{CO} \cdot \text{C}_6\text{H}_2(\text{OMe})_2 \cdot \text{COOH}$ [= 1 : 3 : 4 : 2], is best prepared by treating hemipinimide with sodium hydroxide. It forms hexagonal plates, and, when anhydrous, melts at 142° , probably yielding the imide. A mixture of the α - and β -acids is best separated by dissolving in aqueous ammonia and adding hydrochloric acid when the β -acid separates. The *silver* salt of the β -acid crystallises in colourless needles, is soluble in hot water, and is not rapidly darkened on exposure to light.

Cyanodimethoxybenzoic acid, $\text{CN} \cdot \text{C}_6\text{H}_2(\text{OMe})_2 \cdot \text{COOH}$ [= 6 : 2 : 3 : 1], prepared in the same way as the isomeric acid, crystallises in slender needles which contain $2\text{H}_2\text{O}$, and when anhydrous melts at $81-82^\circ$.

The authors consider that the formation of α -amic acids on treating the anhydride of unsymmetrical dicarboxylic acids (camphoric and hemipinic) with ammonia, and the formation of the isomeric β -amic acids on treating the corresponding imides with caustic soda are readily accounted for on the supposition that one of the carboxylic groups of the dibasic acid has stronger acid properties than the other.

J. J. S.

The Root of *Rumex nepalensis*. By OSWALD HESSE (*Ber.*, 1896, 29, 325).—In consequence of an announcement by A. G. Perkin (*Trans.*, 1895, 1084) of his intention to investigate the substances contained in this root, the author states that he has already obtained the following compounds from it, and is engaged in their examination: (1) $\text{C}_{15}\text{H}_{16}\text{O}_4$, yellow plates, melting at $186-188^\circ$; (2) $\text{C}_{16}\text{H}_{18}\text{O}_4$, orange needles, melting at 136° ; (3) $\text{C}_{18}\text{H}_{18}\text{O}_4$, greenish-yellow prisms,

melting at 158° . The first is soluble in sodium carbonate, the other two are insoluble.

C. F. B.

Metallic Salts with Organic Bases. By FRITZ REIZENSTEIN (*Zeit. anorg. Chem.*, 1896, **11**, 254—263; see also *Abstr.*, 1895, i, 121).—*Tetrapyridine nickelous chloride*, $\text{NiCl}_2 \cdot 4\text{C}_5\text{NH}_5$, is obtained by boiling hydrated nickelous chloride, previously heated for some time at 145° , with an excess of pyridine; the bluish-green mass thus obtained is washed with absolute alcohol and ether. It crystallises from pyridine in bright blue needles.

Pyridine nickelous chloride, $\text{NiCl}_2 \cdot \text{C}_5\text{NH}_5$, is obtained by heating the preceding compound at 115 — 120° .

Tetrapyridine cobaltous chloride, previously prepared from anhydrous cobaltous chloride, can also be obtained by adding pyridine to an aqueous solution of cobaltous chloride; it crystallises from the mixture in deep red crystals. Monopyridine cobaltous chloride is formed on heating the tetrapyridine compound at 115 — 120° , or the dipyridine compound at 104 — 106° ; it is a bright blue powder.

Quinoline cobaltous chloride, $\text{CoCl}_2 \cdot \text{C}_9\text{NH}_7$, is obtained by heating the tetraquinoline compound at 115 — 120° for one hour and then at 120 — 135° for one hour.

Cobalt and nickel sulphate also give compounds with pyridine, which will be described later. Hydrated compounds of the above type have not been obtained; when the monhydrate or dihydrate of cobaltous chloride is treated with pyridine or quinoline, dipyridine or diquinoline cobaltous chloride is obtained.

E. C. R.

Pyridine Alkyl Iodides. By ALBERT B. PRESCOTT (*J. Amer. Chem. Soc.*, 1896, **18**, 91—96).—These compounds are formed on treating pyridine with the required alkyl haloïd, the methyl compound being prepared by heating the mixture in a flask attached to a reflux condenser. The ethyl compound is best prepared by occasionally shaking the mixture in a flask at the ordinary temperature, whilst the propyl compounds are made by heating the mixture in a sealed tube at 130° .

Pyridine methiodide forms flat needles, sometimes aggregated in rosettes, very soluble in water, alcohol, methylic alcohol, chloroform, acetone, and glacial acetic acid, insoluble in ether, benzene, and carbon bisulphide. It is slightly deliquescent and melts at 117° .

Pyridine ethiodide forms colourless plates melting at 90.5° ; it is permanent or slightly deliquescent, soluble in water, alcohol, acetone, and glacial acetic acid, from which it crystallises, and slightly soluble in ethylic acetate, insoluble in ether, benzene, carbon bisulphide, and chloroform.

Pyridine propiodide forms colourless plates and melts at 52 — 53° ; it is deliquescent, soluble in water, alcohol, amyl alcohol, ethylic acetate, and benzene, insoluble in ether and chloroform.

Pyridine isopropiodide forms colourless crystals, soluble in water, 95 per cent. alcohol, and ethylic acetate, but less freely in absolute

alcohol, amylic alcohol, or chloroform, insoluble in ether; it melts at 114—115°.

L. DE K.

Dipyridine Trimethylene Dibromide. By R. F. FLINTERMANN and ALBERT B. PRESCOTT (*J. Amer. Chem. Soc.*, 1896, **18**, 28—35).—The authors have prepared this compound, $\text{CH}_2(\text{CH}_2\cdot\text{C}_5\text{NH}_5\text{Br})_2$, by acting on pyridine (2 mols.), boiling at 116—118°, with trimethylene bromide (1 mol.), with the addition of one-fifth of the volume of absolute alcohol to the mixture. The compound forms completely in about a week in the cold, but is more rapidly obtained by heating in a sealed tube for four hours at 105—110°.

The light brown, crystalline mass is drained, washed with alcohol, and once recrystallised from alcohol, then being nearly white; a pure, white product is, however, obtained when the action takes place in the cold. It is very soluble in water, less soluble in alcohol and ether, and but very slightly so in chloroform. Kept in an open vessel for weeks, it shows no indication of decomposition, only getting slightly moist. The crystals melt and gradually decompose at 225—226°.

The molecular weight was determined by the cryoscopic method, using phenol as solvent.

L. DE K.

Synthesis of Tetrahydropyridine Derivatives and their Conversion into Piperidine Derivatives. By ANDREAS LIPP (*Annalen*, 1895, **289**, 173—253; compare Abstr., 1892, 1243).—Normal acetobutylic alcohol (*hexane-2 : 6-ketol*) has been already described by the author (Abstr., 1886, 218); the *anhydride*, $\text{C}_6\text{H}_{10}\text{O}$, which boils at 106—107° under a pressure of 720 mm., is identical with methyldehydrohexone (Perkin, jun., *Trans.*, 1887, 723). The *phenylhydrazone* of acetobutylic alcohol is obtained from the alcohol itself or the anhydride, and forms a yellowish, viscous oil, which becomes brown on exposure to the air; the *oxime* is a colourless syrup, which has no action on Fehling's solution until treated with sulphuric acid. The *acetate* boils at 231—232° under a pressure of 713 mm., and yields a white, crystalline compound with sodium hydrogen sulphite; the *benzoate* is a limpid, colourless liquid, which decomposes when heated under atmospheric pressure.

Methyl benzamidobutyl ketone, $\text{COMe}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NHBz}$, is obtained by the action of benzoic chloride on Δ^2 -tetrahydropicoline (*loc. cit.*) in presence of alkali; it crystallises in needles and melts at 75—76°. When heated at 170—180° with fuming hydrochloric acid, it is resolved into benzoic acid and tetrahydropicoline. The *oxime* crystallises in needles or prisms and melts at 87°.

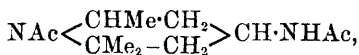
Methyl phenylamidobutyl ketone *platinochloride* crystallises in needles, and at 200—202° decomposes, evolving gas; the *picrate* melts at 124—125°, and the *oxime* at 68—69°, the *phenylhydrazone* being a yellowish, viscous oil. Reduction of the ketone in acid solution gives rise to 1-phenyltetrahydropicoline, whilst, in presence of an alkali, *phenylamidomethylbutylcarbinol*, which melts at 44—45° and boils at 320—322° (720 mm. pressure), is formed.

M. O. F.

The Oximes of the Cyclic Acetone Bases: Paramidotrimethylpiperidine. By CARL D. HARRIES (*Ber.*, 1896, **29**, 521—529).

—*Triacetaminoxime*, $C_9H_{18}N_2O$, is obtained by the action of hydroxylamine on triacetamine, and crystallises in large, white, six-sided prisms, melting at $152-153^\circ$; it forms crystalline salts with hydrochloric and sulphuric acids. *Benzylidenediacetaminoxime*, $C_{13}H_{18}N_2O$, crystallises in lustrous, four-sided tablets, melting at $140-141^\circ$, and is only sparingly soluble in boiling water.

Vinyldiacetaminoxime, $NH < \begin{smallmatrix} CHMe \cdot CH_2 \\ CMe_2 - CH_2 \end{smallmatrix} > C:NOH$, crystallises in translucent, four-sided tablets, melting at $150-151^\circ$. When reduced with alcoholic hydrogen chloride, zinc dust, and a little water, it is converted into 4-amido-2:2:6-trimethylpiperidine, which forms a crystalline mass, melts at $25-26^\circ$, and boils at 60° (pressure = 7.5 mm.). The base has a faint odour of piperidine, and rapidly combines with the carbonic anhydride of the air, forming a carbamate. The *hydriodide* of the base crystallises in fascicular groups of white prisms, and is moderately soluble in water; the *hydrochloride* is readily soluble in water; the *aurochloride* crystallises in red, oblique, six-sided tablets, and is sparingly soluble in water, whilst the *platinochloride* and *picrate* are also crystalline. The base forms both a *normal* and an *acid oxalate*, the latter being very hygroscopic. 4-Acetamido-2:2:6-trimethylpiperidine crystallises in cubes, melting at $206-207^\circ$; it is strongly basic, and forms an *aurochloride*, melting at 235° with decomposition. The *diacetyl compound*,



is formed when the base is heated with excess of acetic anhydride at 160° ; it forms small prisms, melts at $88-89^\circ$, boils at $160-170^\circ$ (pressure = 8 mm.), and has basic properties, forming a crystalline *aurochloride*. This diacetyl compound is accompanied by another basic substance, which boils at about 200° (pressure = 8 mm.), and is probably an anhydro-derivative. The base does not yield a diazo-compound with sodium nitrite and an acid, whilst with amyl nitrite it yields a nitroso-derivative, the imido-group having taken part in the reaction. When heated with chloroform and alcoholic potash, no carbylamine derivative is produced. The base reacts with carbon bisulphide, forming a *thiocarbamate*, $C_9H_{18}N_2S_2$, which crystallises from water in prisms and melts at $187-188^\circ$. When this salt is treated with mercuric chloride, it yields the hydrochloride of a new base. The latter crystallises in small prisms and melts at $79-80^\circ$. It has not the smell or other properties of a thiocarbimide, and prob-

ably has the constitution $N < \begin{smallmatrix} CHMe \cdot CH_2 \\ CS - NH \\ CMe_2 - CH_2 \end{smallmatrix} > CH$.

A. H.

Isopipecoline. By ALBERT LADENBURG (*Ber.*, 1896, **29**, 422-424). —The reasoning is given that led the author to regard as isopipecoline what Marckwald (this vol., i, 253) asserts to be merely a mixture of *d*- and *l*-pipecoline. The author maintains that his own conclusion is correct.

C. F. B.

Derivatives of Pipecolinic acid. By RICHARD WILLSTÄTTER (*Ber.*, 1896, **29**, 389—392).—Ethylic pipecolinate, $\text{COOEt} \cdot \text{C}_5\text{NH}_{10}$, is prepared from *nitroscpipecolinic acid*, which is oily; it is a colourless, highly refractive, viscid liquid, with an odour resembling that of acetamide; it boils at $216\text{--}217^\circ$ (corr.), and at 107° under a pressure of 20 mm., has a strongly alkaline reaction, is volatile at the ordinary temperature, and miscible with alcohol, water, and ether. In presence of dilute sulphuric acid, the ethylic salt slowly decomposes potassium permanganate, and is extremely readily hydrolysed. H. Meyer's description of it is incorrect. The yield is 90 per cent. of the theoretical. The acid melts at 264° , and has a neutral reaction; Ladenburg states that it has an acid reaction, and melts at 259° . Unless diluted, methylic iodide and ethylic pipecolinate react with explosive violence, ethylic pipecolinate hydriodide, ethylic methylpipecolinate, and *ethylic n-methylpipecolinate methiodide* being formed; the latter crystallises in colourless prisms, melts at $127\text{--}128^\circ$, and, when distilled, is resolved into its constituents. It is readily soluble in soda, and is hydrolysed, but not otherwise decomposed, when the solution is boiled; when fused with potash, it yields dimethylamine, but the reaction proceeds with difficulty; its stability under these conditions is in marked contrast to the corresponding derivatives of tropinic acid, ecgonine, and anhydroecgonine, which also contain a reduced pyridine ring (compare this vol., i, 265). The *aurochloride* of the *methochloride*,



crystallises in thin, flat, yellow plates melting at 78° . The corresponding salt of the *acid* crystallises in golden, lustrous, tetragonal plates and prisms, melting and decomposing at $227\text{--}228^\circ$.

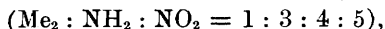
J. B. T.

3-Nitroquinoline and 3-Amidoquinoline. By ADOLPH CLAUS and LUDWIG SCHNELL (*J. pr. Chem.*, 1896, [2], **53**, 106—126).—Contrary to expectation, 3-nitroquinoline could not be directly nitrated to a dinitroquinoline. When dry hydrogen bromide is passed into the chloroform solution of 3-nitroquinoline, the *hydrobromide*, $\text{NO}_2 \cdot \text{C}_9\text{NH}_6 \cdot \text{HBr}$, separates in the form of a heavy, white, crystalline powder melting at 245° , and at the same time losing hydrogen bromide. By shaking this salt with bromine in chloroform, the *dibromide*, $\text{NO}_2 \cdot \text{C}_9\text{NH}_6 \cdot \text{HBr} \cdot \text{Br}_2$, is obtained; it forms yellowish-red crystals, and is converted into 3': 3-bromonitroquinoline when heated at $170\text{--}180^\circ$ until the hydrogen bromide is almost entirely expelled. The bromonitroquinoline crystallises from hot water in yellowish needles, melts at 165° , and sublimes; the *methiodide* crystallises from hot water in brilliant, red needles, and melts at 235° . The bromo-derivative shows the same resistance to nitration that is exhibited by the parent nitroquinoline; justification for the adopted orientation is given. 3: 3'-Bromamidoquinoline is best prepared by mixing the nitro-compound with water and the calculated quantity of iron powder, so as to form a thick paste, which is then thoroughly mixed with a few drops of glacial acetic acid; after the action is over, a porous mass is left, from which the amido-compound is extracted by chloroform or ether. It crystallises in colourless needles, melts at

106°, is not volatile with steam, and dissolves freely in hot water or alcohol; its salts are yellow. By brominating the amido-derivative in chloroform, 4 : 3' : 3-dibromamidoquinoline is obtained in the form of a *hydrobromide* (m. p. 210°), from the solution of which it may be precipitated by alkalis; it crystallises in slender, lustrous needles, which are greenish in mass, and melts at 146°; evidence of the orientation is given.

3-Amidoquinoline melts at 114°, not 140° (Bielstein, *Org. Chem.*, **3**, 752); the *methiodide* is obtained as a yellow, crystalline precipitate, and melts at 199°. By acetylsing 3-amidoquinoline, 3-acetamidominoquinoline is formed; it crystallises in silky, colourless, slender needles, melts at 75°, sublimes unchanged, and dissolves freely in water and alcohol, but only sparingly in benzene, light petroleum, &c. 3-Benzamidoquinoline crystallises in brilliant, colourless laminae, melts at 130°, and dissolves easily in hot alcohol; it sublimes unchanged, but is not volatile with steam. 2:3-Bromamidoquinoline, prepared by brominating the amidoquinoline in glacial acetic acid, crystallises in colourless laminae, melts at 67°, does not sublime unchanged, and is not volatile with steam; it dissolves easily in alcohol, but only sparingly in hot water; evidence of its orientation is given. 2:3-Bromacetamidominoquinoline is obtained by brominating acetamidominoquinoline; the *hydrobromide* separates first in yellow crystals, which melt at 241°; the base crystallises from hot water in brilliant, bronze coloured laminae, and melts at 165°. *Dibromo-3-amidoquinoline* melts at 170°, and *dibromo-3-acetamidominoquinoline* at 159°; the orientation of the second bromine atom in these two compounds is not yet ascertained. A. G. B.

3-Methylindazole. By SIEGMUND GABRIEL and ROBERT STELZNER (*Ber.*, 1896, **29**, 303—309).—When nitrometaxylylidine,



is treated with sodium nitrite in presence of dilute sulphuric acid, it is converted into 1 : 3-nitromethylindazole, $\text{NO}_2 \cdot \text{C}_6\text{H}_2\text{Me} < \begin{smallmatrix} \text{CH} \\ | \\ \text{N} \end{smallmatrix} > \text{NH}$.

This substance was first obtained by Müller (*Diss. Berlin*, 1883), who, however, ascribed to it the formula $\text{C}_8\text{H}_8\text{N}_3\text{O}_2$. When it is reduced with tin and hydrochloric acid, it yields 4 : 1 : 3-chloramidomethylindazole, which crystallises in plates with a satiny lustre, and melts at 195°, whilst the *acetyl derivative* melts at 154°. When reduced with ammonium sulphide, on the other hand, the nitro-compound is converted

into 1 : 3-amidomethylindazole, $\text{NH}_2 \cdot \text{C}_6\text{H}_2\text{Me} < \begin{smallmatrix} \text{CH} \\ | \\ \text{N} \end{smallmatrix} > \text{NH}$,

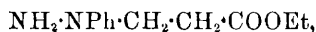
which crystallises in colourless needles, and melts and decomposes at 172°. The base dissolves both in acids and alkalis, and forms a *picrate*, which melts and decomposes at 183°. The *dibenzoyl derivative* forms yellow crystals, and melts at 186—187°. 3-Methylindazole crystallises in slender, colourless needles, melts at 116—117°, and boils at 293—294° (pressure = 747 mm.). The *nitrosamine*, $\text{C}_8\text{H}_7\text{N}_3\text{O}$, forms yellow needles, which melt at 61°, and give Liebermann's reaction. *Methylindazole picrate* melts at 159—160°.

The chlorinated bases formed by the reduction of nitro-com-

pounds by means of hydrochloric acid and tin or stannous chloride, are usually para-derivatives. Ortho-compounds may, however, be formed when the para-position is occupied. It is probable that the formation of these compounds is preceded by the production of a hydroxylamine derivative, and this reacts with the acid, yielding a chloride, which then passes by intramolecular change into a para-chloro-derivative. A. H.

Rejoinder to R. von Rothenburg: Isomerism in the Pyrazole Series. By LUDWIG KNORR (*J. pr. Chem.*, 1896, [2], 53, 127—132). —Polemical (compare Abstr., 1895, i, 303, 395, 571). A. G. B.

Constitution of 1-Phenylpyrazolone. By CARL D. HARRIES and GEORGE LOTH (*Ber.*, 1896, 29, 513—520).—*Ethyl β-anilidopropionate*, $\text{NHPh}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{COOEt}$, is readily obtained by heating ethyl β-iodopropionate with aniline; it is a light yellow oil, which boils at 175° (pressure = 18 mm.). *Ethyl nitroso-β-anilidopropionate* is an oil, which gives Liebermann's reaction. When the nitroso-compound is dissolved in ether and reduced with aluminium amalgam, it is converted into *ethyl α-β-phenylhydrazidopropionate*,



which boils at 174—175° (pressure = 9 mm.), and is readily soluble in dilute alkalis and mineral acids. The *picrate* crystallises in fascicular needles melting at 131—132°. The *oxalate* melts at 107°, and is readily soluble in water. The oxalate reacts with potassium cyanate to form the *semicarbazide of the hydrazido-compound*; this crystallises in cubic crystals melting at 163—164°, and is insoluble in acids and alkalis. The *phenylthiosemicarbazide* melts at 71—74°.

When ethyl phenylhydrazidopropionate is treated with alcoholic sodium ethoxide, it is converted into 1:3-phenylpyrazolidone, $\text{NPh}\begin{smallmatrix} \text{CH}_2\cdot\text{CH}_2 \\ | \\ \text{NH}\cdot\text{CO} \end{smallmatrix}$, melting at 119—121°. The *hydrochloride* of this substance crystallises in nacreous plates melting at 163°. 2:1:3-*Acetylphenylpyrazolidone* crystallises in colourless prisms melting at 66—67°. When phenylpyrazolidone is treated with sodium nitrite, the solution neutralised with ammonia, and silver nitrate added, a yellow substance is obtained, which, however, is not homogeneous, but a mixture of the silver salts of 1:3-phenylpyrazolone and of nitrophenylpyrazolone, produced by the action of traces of nitric acid. The 1:3-phenylpyrazolone obtained from the phenylpyrazolidone melts at 153°, and forms a hydrochloride, which crystallises in slender needles melting at 111°. It was found impossible to prepare the 1-phenylpyrazolone-4-azobenzene described by Rothenburg (Abstr., 1894, i, 145). (4-?) *Nitro-1:3-phenylpyrazolone* is formed when phenylpyrazolone is dissolved in dilute nitric acid, and crystallises in long, thread-like needles melting at 190—192°. 2:1:3-*Acetylphenylpyrazolone* crystallises in colourless, fan-shaped needles melting at 62—63°. A. H.

Action of Hydrazine and Phenylhydrazine on 1 : 4-Diketones. By ALEXANDER SMITH [and in part JAMES H. RANSOM] (*Annalen*, 1896, **289**, 310—337).—3 : 4 : 6-Triphenyldihydropyridazine, $\text{CPh} \begin{smallmatrix} \text{CPh-NH} \\ \text{CH:CPh} \end{smallmatrix} \text{NH}$, is obtained by acting on desylacetophenone with hydrazine for one hour; it crystallises in yellow needles and when heated rapidly melts at 186—188°, decomposing at 190°. Along with this substance there is produced the *monhydrazone* of desylacetophenone, which is also formed when the pyridazine derivative is heated with glacial acetic acid; it crystallises from alcohol in slender needles, and melts at 168°, yielding when distilled, a *compound* which crystallises in white needles, and melts at 181°.

3 : 4 : 6-Triphenylpyridazine, $\text{CPh} \begin{smallmatrix} \text{CPh-N} \\ \text{CH:CPh} \end{smallmatrix} \text{N}$, crystallises in lustrous, white plates, and melts at 171°; it is easily obtained when the dihydro-derivative is distilled, or oxidised with chromic and acetic acids. The substance is also formed during the preparation of triphenyldihydropyridazine, and may be produced by adding potassium nitrite to a solution of the latter compound in cold glacial acetic acid.

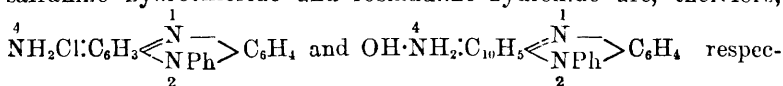
With JAMES H. RANSOM.—The *hydrazone* of phenacyldesoxypiperonin (*Abstr.*, 1893, i. 219), $\text{C}_{30}\text{H}_{22}\text{N}_2\text{O}_4$, crystallises in yellow needles, and melts at 166°.

1 : 3 : 4 : 6-Tetraphenyldihydropyridazine, obtained by the action of phenylhydrazine on desylacetophenone (*Trans.*, 1890, 647), has been regarded by Klingemann as having the constitution of an anilidopyrroline derivative, $\begin{smallmatrix} \text{CH:CPh} \\ \text{CPh:CPh} \end{smallmatrix} \text{N} \cdot \text{NHPh}$, because phenylhydrazine converts $\alpha\beta$ -dibenzoylstilbene into anilidotetraphenylpyrroline (*Abstr.*, 1892, 995); the author describes experiments, however, which are in agreement with the pyridazine formula. The *benzoyl* derivative, $\text{C}_{33}\text{H}_{26}\text{N}_2\text{O}$, crystallises from glacial acetic acid in white needles, and melts at 139—140°; it is indifferent towards phenylhydrazine, alcoholic potash, and hydrochloric acid. An additive *compound*, $\text{C}_{28}\text{H}_{23}\text{N}_3\text{O}_2$, obtained from tetraphenyldihydropyridazine by the action of nitrous acid, crystallises in pale yellow needles which melt and decompose at 262°; boiling alcoholic potash converts it into a *compound* which crystallises in rhombohedra melting at 133°, and is identical with the substance obtained by the action of acetic chloride on triphenyldihydropyridazine. Tetraphenyldihydropyridazine is indifferent towards sodium in ethylic alcohol, but is reduced in presence of boiling amyl alcohol, yielding two *compounds* which melt at 212° and 157° respectively; the absence of aniline among the products has been established. Boiling dilute nitric acid converts tetraphenyldihydropyridazine into the *compound* $\text{C}_{26}\text{H}_{21}\text{N}_3\text{O}_3$, which melts and decomposes at 255°.

1 : 3 : 4-Triphenylpyrazole is obtained by the dry distillation of 1 : 3 : 4 : 6-tetraphenyldihydropyridazine; it crystallises from glacial acetic acid in small prisms, and melts at 185°. This substance does not arise from the decomposition of an anilidopyrroline derivative, because neither triphenylpyrroline nor aniline is found in the distil-

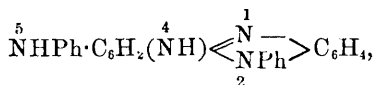
late; the gas produced during distillation, moreover, is free from ammonia, and contains but little nitrogen. M. O. F.

Indulines and Safranines. By OTTO FISCHER and EDUARD HEPP (*Ber.*, 1896, **29**, 361—371; compare this vol., i, 50, and Kehrman, *Abstr.*, 1895, i, 527).—The indulines and safranines are readily differentiated by their behaviour towards concentrated sulphuric acid, the former giving violet or blue colours, whilst the simple safranines all dissolve with a green coloration. The bye-products obtained in the preparation of indazine and phenylmauveine (*Abstr.*, 1895, i, 608) are probably true indulines, as they dissolve with a blue colour in sulphuric acid. Objection is taken to Kehrman's view that salts of indulines and indone (rosinduline) are derived from the orthoquinoidal azonium form, whilst the induline bases, free from oxygen and the indones, are paraquinoidal anhydrides of amido- or hydroxy-azonium bases. The basicity of many of these compounds must be due to the imido-group and not to the phenazine nitrogen, otherwise it is difficult to understand the feebly basic properties of aposafranone and rosindone which form no acetates, but contain the group NPh; the azonium formula also indicates the presence of a free amido-group in the salts of aposafranine and rosinduline, but the former do not react with nitrous acid, aldehydes, or ketones. No special significance can be attached to the formation of hydrates by the above compounds, as this property is common to many organic bases; rosaniline and rosinduline hydrates closely resemble one another, the former is converted into the anhydrous compound by heating at 40—50°, or when extracted with ether or benzene from its aqueous solution. The formulæ of aposafranine hydrochloride and rosinduline hydroxide are, therefore,



tively.

It has been previously shown (*Abstr.*, 1893, i, 613) that "benzene-induline," $\text{C}_{18}\text{H}_{13}\text{N}_3$, and "phenylinduline," $\text{C}_{24}\text{H}_{17}\text{N}_3$, are formed by the interaction of aposafranine salts and aniline; these compounds have now been identified as *anilidoaposafranine*,



and *anilidophenylaposafranine*, ${}^5\text{NPh}\cdot\text{C}_6\text{H}_2(\text{NPh})\left\langle\begin{smallmatrix} \text{N}^1 \\ \text{NPh}^2 \end{smallmatrix}\right\rangle\text{C}_6\text{H}_4$. The former crystallises from dilute alcohol; by the action of acids, it yields anilidoaposafranone, ${}^5\text{NPh}\cdot\text{C}_6\text{H}_2\text{O}\left\langle\begin{smallmatrix} \text{N}^1 \\ \text{NPh}^2 \end{smallmatrix}\right\rangle\text{C}_6\text{H}_4$, and then

hydroxyaposafranone, $\text{OH}\cdot\text{C}_6\text{H}_2\text{O}\left\langle\begin{smallmatrix} \text{N}^1 \\ \text{N}^2 \end{smallmatrix}\right\rangle\text{C}_6\text{H}_4$, which was previously termed "benzeneindonehydrate." The *methoxy*-derivative crystallises

in red, stellate needles or well developed prisms, melts at 246—248°, and gives an orange solution with concentrated sulphuric acid. Anilidophenylaposafranine is formed in considerable quantity from aniline and aposafranine under the conditions previously given, but only in traces if alcohol is present. Paratoluidine and aposafranine, in the absence of alcohol, yield paratoluidoaposafranine and *toluido-tolylaposafranine* which, from its resemblance to the phenyl derivative, should have a similar constitution; it crystallises in green, lustrous plates, and melts at 238—240°.

Paraphenylenediamine and aposafranine, in presence of alcohol, yield the compound $\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \overset{5}{\text{N}}\text{H} \cdot \text{C}_6\text{H}_2(\overset{4}{\text{NH}}) \left\langle \overset{1}{\text{N}} \text{---} \text{N}^{\text{2}} \text{Ph} \right\rangle \text{C}_6\text{H}_4$, which

crystallises from benzene in bluish-green prisms, melts and decomposes at 227°, and gives, with concentrated sulphuric acid, a reddish-violet coloration which changes to red on dilution. The *hydrochloride* is crystalline, and, in aqueous solution, has a brownish-red colour. By the action of dilute sulphuric acid at 170°, the base is resolved into paraphenylenediamine and hydroxyaposafranine.

Orthophenylenediamine and aposafranine hydrochloride yield *phenylfluorindine*, $\text{C}_6\text{H}_4 \left\langle \text{NH} \text{---} \text{N} \right\rangle \text{C}_6\text{H}_2 \left\langle \overset{1}{\text{N}} \text{---} \text{N}^{\text{2}} \text{Ph} \right\rangle \text{C}_6\text{H}_4$, the formation of which is probably preceded by that of a compound isomeric with the preceding; it is very sparingly soluble, and crystallises from ethylic benzoate in needles of a golden bronze lustre; in mineral acids, the solution is blue, with a bluish-red fluorescence. The *hydrochloride* is crystalline, and its alcoholic solution is blue, with a red fluorescence. This synthesis confirms the authors' formulæ previously given to the fluorindines.

The preparation of anilidophenylaposafranine has been already described (see above); it is also formed from aniline and anilidoaposafranine, by the oxidation of azophenine, and by the elimination of the amido-group from "amidophenylinduline." The molecular weight in naphthalene agrees with the above formula; the earlier determinations were made in benzene solution, and the results were too low. The *nitrate* crystallises in green, lustrous prisms. Amido-

phenylinduline, $\overset{5}{\text{NHPh}} \cdot \text{C}_6\text{H}_2(\overset{4}{\text{NPh}}) \left\langle \overset{1}{\text{N}} \text{---} \text{N}^{\text{2}} \text{Ph} \right\rangle \text{C}_6\text{H}_3 \cdot \overset{4}{\text{NH}_2}$, has been pre-

viously described, but the position of the amido-group was not determined; this has now been accomplished (see below). The *hydrochloride* and *nitrate* crystallise with $\frac{1}{2}$ and $1\text{H}_2\text{O}$ respectively. By the action of dilute sulphuric acid at 170° on the base, amido-hydroxyaposafranine (this vol., i, 50) is formed; the *nitrate* crystallises in thick, greenish, lustrous prisms; the *diazo*-derivative yields hydroxyaposafranone when heated. With dilute sulphuric acid at 230—250°, amidophenylinduline yields *dihydroxyaposafranone*, which crystallises in brownish-yellow needles, melts above 280°, and dissolves in soda with a reddish-yellow coloration. With alkalis, amidophenylinduline yields hydroxyaposafranone, which was identified as "safranin" by means of the methoxy-derivative, which softens at

240° and melts at 266°, not at 240° as previously stated. A second base, probably *anilidosafraanol*, is also formed in small quantity; it crystallises in blue, lustrous prisms, and, like anilidoaposafranone, dissolves in concentrated sulphuric acid, yielding a dull green solution which changes successively to green and violet-red when diluted. The *hydrochloride* is green, lustrous, and crystalline. The constitution of amidophenylinduline (anilidomauveïne), as regards the position of the amido-group, is shown by the following facts: It is formed by the fusion of amidoazobenzene, and from azophenine and paraphenylenediamine; phenosafranine, mauveïne, phenylmauveïne, and amidophenylinduline hydrochlorides by the action of aniline, yield the same induline (m. p. 286—288°), which is the final product of the action of aniline on amidoazobenzene, phenylamidoazobenzene, and azobenzene. The *acetate* of this *induline* crystallises in characteristic, flat prisms of a coppery bronze lustre. The *hydrochloride* and *hydrobromide* have also been prepared. The formula of the induline is probably $C_{42}H_{32}N_6$, as, in its formation from amidophenylinduline and phenylmauveïne

the primary product is probably $N^4Ph \cdot C_6H_3 \cdot \begin{smallmatrix} N^1 \\ \diagup \quad \diagdown \\ N^2 \end{smallmatrix} > C_6H_3 \cdot N^4HPh$, which

melts at 245°, has been previously described, and yields a soluble *acetate*.
J. B. T.

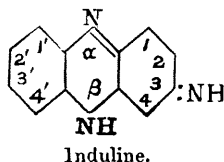
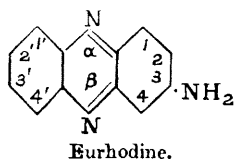
Safranines. By GEORGE F. JAUBERT (*Compt. rend.*, 1895, 121 947—948; compare *Abstr.*, 1895, i, 219 and 278).—The oxidation of a mixture of paraphenylenediamine and methylmetaphenylenediamine yields the methyl derivative of phenylene-red, but if metatolylenediamine is substituted for the methylmetaphenylenediamine,

the dimethylsafranine, $NH \cdot C_6H_2Me \cdot \begin{smallmatrix} N^4 \\ \diagup \quad \diagdown \\ N^5Me \end{smallmatrix} > C_6H_3 \cdot N^4H_2$, is obtained in

considerable quantity. It has all the characteristic properties of the safranines, dyes mordanted cotton a ponceau red, and yields a diazo-derivative with nitrous acid. The diethyl derivative is obtained in a similar way, and the ethylsafranil is prepared by the action of nitrosophenol on ethylmetamidophenol.

α - and β -naphthasafranols are obtained by the action of nitrosophenol on metahydroxyphenyl- α -naphthylamine, or the β -derivative. If the sulphonic derivative of metahydroxydiphenylamine is used, phenosafranolsulphonic acid is formed.
C. H. B.

Nomenclature of Phenazine Dyes. By GEORGE F. JAUBERT (*Ber.*, 1896, 29, 414—418).—The phenazine derivatives can be divided into two classes: eurhodines, with an orthoquinonoid structure, and indulines, with a paraquinonoid structure.



Eurhodines.—The derivative, with an additional NH_2 in 3', is to be called amidoeurhodine ("phenylene-red"). When the NH_2 of eurhodine is replaced by OH, the new compound is to be called *eurhodol*; amido- and hydroxy-eurhodol have, in addition, NH_2 and OH respectively in 3'.

Indulines.—The 3'-amido-derivative, amidoinduline, is the simplest possible "safranine." If the NH of induline is replaced by O, the compound is to be called *indulone*; amido- and hydroxy-induline ("safranin") have, in addition, NH_2 and OH respectively in 3'. Substitution of the H of the NH-group in the middle ring is to be indicated by the vowel o; thus, phenoindulone ("safranone"). In phenylindulone some other hydrogen atom would be replaced by phenyl.

It is pointed out that in order to get a "safranine" dye from an induline derivative it is necessary that the amido-group should go into the *para*-position relatively to the α -nitrogen atom, just as, in order to get a pararosaniline compound from diamidotriphenylmethane, the third amido-group must go to the *para*-position relatively to the methane carbon atom.

C. F. B.

Dithiazolic Derivatives. By CHARLES LAUTH (*Compt. rend.*, 1895, 112, 1152—1154).—The compound $\text{C}_6\text{H}_4 < \text{S} \text{N} > \text{C} \cdot \text{C} < \text{S} \text{N} > \text{C}_6\text{H}_4$, obtained by Hofmann by heating acetanilide with sulphur, contains two groups $< \text{S} \text{N} > \text{C}$, and might, therefore, be expected to yield colouring matters similar to the primulines. When treated with a mixture of nitric and sulphuric acids, it yields a mixture of two isomeric dinitro-derivatives, one of which melts at about 210° and the other at about 290° , and this, when reduced by stannous chloride in presence of an acid at 60 — 100° , yields two isomeric diamido-derivatives, which can be separated by the difference in their solubility in water. The less soluble of the two shows brilliant, green fluorescence in alcoholic solution; the other is non-fluorescent. Both the bases and their salts alter when their solutions are boiled, hydrogen sulphide being liberated. Hydrogen sulphide is also evolved when the bases are treated with an acid reducing agent.

Both bases are dyes, and impart a beautiful, yellow colour to animal fibres, and also to unmordanted cotton. Their diazo-derivatives also yield a varied series of colouring matters, which dye unmordanted cotton; β -naphthol- α -sulphonic acid, for example, yields a red dye with the diazo-derivative of the soluble base, and amido- α -naphtholdisulphonic acid yields a blue dye with the diazo-derivative of the less soluble base. The colours on fabrics are somewhat resistant to the action of acids and alkalis, but fade when exposed to light.

C. H. B.

Constitution of Tropine. By ALBERT LADENBURG (*Ber.*, 1896, 29, 421—422).—Willstätter (this vol., i, 265) has misunderstood the author's reasoning; he would not otherwise maintain that tropinic acid contains a pyridine ring with a tertiary nitrogen atom, whilst

the author has shown it to form an open chain with a secondary nitrogen atom. C. F. B.

Tropinone. By RICHARD WILLSTÄTTER (*Ber.*, 1896, **29**, 393—403).—*Tropinone*, $\text{CH} \begin{array}{c} \text{CH}_2\text{--CH}_2 \\ \text{CO--CH}_2 \\ \text{CH}_2\text{--NMe} \end{array} \text{CH}$, is prepared by the cautious

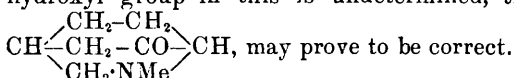
oxidation of tropine by means of chromic anhydride in glacial acetic acid solution; it is colourless, soon turns yellow when exposed to air, but is stable towards potassium permanganate; it is readily soluble, and volatile at the ordinary temperature, and distils readily with steam if the solution contains free potash; it has a characteristic basic odour, forms flat crystals, melts at $41\text{--}42^\circ$, and boils at $224\text{--}225^\circ$ (corr.). Tropine boils at 233° (corr.). The ketone is an active base, and liberates ammonia from its salts; it forms white clouds with hydrogen chloride, and, like granatone, gives a mirror with silver nitrate; it precipitates the hydroxides from copper, ferric, and aluminium salts, and with lead nitrate gives a flocculent precipitate, which becomes granular and crystalline when warmed, and dissolves readily in hot water. With phosphomolybdic acid, a greenish-yellow, flocculent precipitate is formed; with tannin, a white one; with potassium dichromate and sulphuric acid, a green coloration is obtained. The yield is 80 per cent. of the theoretical.

The *mercuroidide* crystallises in long, silky, lustrous needles; the *potassioiodide* is at first brown and oily, but readily crystallises in prisms. The *hydrochloride* crystallises in lustrous, stellate prisms, melting and decomposing at $188\text{--}189^\circ$. The *picrate* is deposited in long, lustrous, yellow needles, melting and decomposing at 220° ; it is conveniently employed for the purification of tropinone. Tropine picrate is more readily soluble than the preceding compound, is strongly pleochroic, and gradually decomposes when heated. *Tropinone platinochloride* crystallises at the ordinary temperature in orange-red pyramids, and from hot solutions in feathery aggregates of prisms, melting and decomposing at $191\text{--}192^\circ$. The *aurochloride* is deposited in tabular aggregates of sulphur-yellow, microscopic prisms: it melts and decomposes at $160\text{--}170^\circ$, and, when boiled with water, deposits gold. The *phenylhydrazone* is oily. The *methiodide* forms highly refractive, crystalline aggregates, resembling those of sodium chloride, and melts and decomposes at $263\text{--}265^\circ$; when boiled with sodium carbonate, it is readily converted into dimethylamine and dihydrobenzaldehyde; the same products are obtained by treating the methiodide with silver oxide and boiling the resulting *tropinonemethylammonium hydroxide*, which is strongly alkaline. The dihydrobenzaldehyde appears to be identical with Einhorn's $\Delta^{4,6}$ -compound from anhydroecgonine dibromide. The *aurochloride* of *tropinone methochloride* crystallises in yellow prisms, melting and decomposing at $205\text{--}206^\circ$.

Tropinone oxime crystallises from light petroleum in slender, stellate prisms, melting at $111\text{--}112^\circ$. It has both basic and feebly acidic properties, and readily reduces silver salts when warmed with them. The *hydrochloride* crystallises in prisms and melts and decomposes at 242° . The *methiodide* is deposited in long, colourless, highly refractive

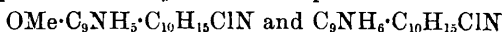
prisms; it melts at 236° , but a portion decomposes previously, and is more stable than tropinone methiodide, as it is not decomposed when boiled with alkali. The *aurochloride* of the *methochloride* crystallises in slender, pale yellow prisms, melting and decomposing at 182° . The *ammonium hydroxide* reduces silver salts, but is not decomposed by alkali.

The preceding results are in complete accord with Merling's formula for tropine, but not with Ladenburg's, which indicates that it is a primary alcohol (compare this vol., i, 65). The relationship of tropine to tropinone and tropinic acid is similar to that of borneol to camphor and camphoric acid, and tropinone shows a striking analogy with granatonine, $C_9H_{15}NO$ (Tanret's pseudopelletierine), both in general properties and derivatives; granatonine methiodide, for example, yields, by the action of alkali, dihydroacetophenone. The formula given above for tropinone corresponds with that regarded by Merling as the more probable for tropine, but, as the position of the hydroxyl group in this is undetermined, the alternative formula,

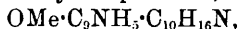


J. B. T.

Replacement of the Hydroxyl Group in Cinchona Alkaloids by Hydrogen. By WILHELM KOENIGS (*Ber.*, 1896, 372—374; compare this vol., i, 264).—Quinine and cinchonidine, when treated with phosphorus pentachloride, yield the compounds



respectively, from which, by the action of iron filings and dilute sulphuric acid at the ordinary temperature, *deoxyquinine*,



and *deoxycinchonidine*, $\text{C}_9\text{NH}_6\cdot\text{C}_{10}\text{H}_{15}\text{N}$, are formed. No anhydro-bases are produced, as in the case of cinchonine. Deoxyquinine crystallises from ether or dilute alcohol with $2\frac{1}{2}\text{H}_2\text{O}$, in colourless, slender needles, melts at about 52° , and deliquesces over sulphuric acid; in dilute solution, it fluoresces like quinine. The salts are readily soluble, and crystallise with difficulty; the *platinochloride* darkens without melting, at 260° . The *hydriodide* is crystalline. Deoxycinchonidine crystallises in colourless, rhombic plates, and melts at 61° . The *platinochloride*, *zincchloride*, *cadmiocchloride*, and *mercurichloride* crystallise readily in needles. Both bases give the quinine reaction with chlorine water and ammonia. Quinine and cinchonidine are levorotatory, conquinine and cinchonine dextrorotatory; all four chlorides are dextrorotatory, as are the anhydro-bases quinenine, cinchonidenine, quinidenine, and cinchenine, but the sign of rotation of the deoxy-bases is the same as that of the alkaloids from which they are derived; these facts accord with Pasteur's view, that the alkaloids contain two asymmetric carbon atoms in the "second half" of the molecule; to one of these the hydroxyl group is probably linked, and, as the deoxy- and anhydro-bases differ in the sign of their rotation, this carbon atom must be a tertiary one.

J. B. T.

Organic Chemistry.

Investigations on American Petroleum. Chemistry of the Berea Grit Petroleum. By CHARLES F. MABERY and ORTON C. DUNN (*Amer. Chem. J.*, 1896, **18**, 215—235).—Analyses of the Berea Grit sandstone: I, white oil sand; II, blue caprock, yield the following figures.

	SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	CaO. MgO.	H ₂ O (combined)	Total.
I.	92.30	4.80	0.92	0.28	1.40	99.70
II.	91.80	4.60	1.50	0.34	1.80	100.04

Samples of oils obtained from the principal sandstones of the lower coal measures which overlie the Berea Grit sandstone, namely, from the 140, 300, 500, and 700 foot strata, were collected in fractions of 25°, and the percentage of distillate, specific gravity, bromine absorption, and hydrogen bromide eliminated, determined in each case.

Three specimens of the Berea Grit petroleum from the 1,500 foot oil sand were treated in the same manner, and two analyses of gas evolved from this formation were made.

	CO ₂ .	CO.	O.	N.	Illuminating hydrocarbons.	CH ₄ .	Total.
I.	0.30	0.40	4.00	1.20	2.60	92.00	99.70
II.	0.10	0.80	0.30	1.00	0.70	97.00	99.90

The fractionation of this oil yielded a hydrocarbon, C₁₀H₂₂, boiling at 162—163° (760 mm.), and of sp. gr. = 0.7475 at 20°. Another hydrocarbon of this formula was also isolated, boiling at 173—174°, and with a sp. gr. = 0.7517 at 20°.

A hydrocarbon, C₁₁H₂₄, was obtained from the fraction 194—196°. This boils at 195° (760 mm.), and has a sp. gr. = 0.7622 at 20°.

From the higher fractions, a hydrocarbon, C₁₂H₂₆, boiling at 215° (760 mm.), of sp. gr. = 0.7746, was isolated. J. F. T.

Artificial Production of Asphalt from Petroleum. By CHARLES F. MABERY and J. H. BYERLEY (*Amer. Chem. J.*, 1896, **18**, 141—150).—In the ordinary process of distilling petroleum, the residue is a porous coke. The authors describe a process, originated by F. X. Byerley, for obtaining more valuable products by slow distillation in a current of air at a temperature not exceeding 650° F. In this way, asphalts of various degrees of viscosity (some of which closely resemble native bitumen) are formed, but no free carbon.

In a note on the determination of sulphur in organic substances by combustion in air (compare Mabery, *Abstr.*, 1895, ii, 136), it is stated that substances containing a high percentage of sulphur yield sulphurous as well as sulphuric acid. In these cases, a little hydrogen peroxide should be added before titration. A. E.

Action of Hydrogen Bromide on Hydrocarbons of the Series C_nH_{2n-2} . By WLADIMIR IPATIEFF (*J. pr. Chem.*, 1896, [2], 53, 145—168).—The main product of the action of a glacial acetic acid solution of hydrogen bromide on dimethylisoallylene (b. p. 39·5—41°) cooled to 0° is β -dimethyltrimethylenic dibromide, $CMe_2Br\cdot CH_2\cdot CH_2Br$; it boils at 74—75°, and its sp. gr. = 1·6975 at 0°/0°; its constitution was ascertained by converting it into a glycol, which proved to be identical with that prepared by Kondakoff from a corresponding dichloride (*Abstr.*, 1893, i, 541). A closed chain hydrocarbon is obtainable from this dibromide, and will be treated of hereafter.

The hydrocarbon, C_6H_{10} , obtained by heating the bromohexylene, $CMe_2\cdot CBr\cdot CH_2Me$, which boils at 138—141°, with alcoholic alkali in a sealed tube at 150°, may be trimethylisoallylene, $CMe_2\cdot C\cdot CHMe$, or methylisopropylacetylene, $CHMe_2\cdot C\cdot CMe$, since Faworsky has shown that conversion of such a hydrocarbon into a disubstituted acetylene is frequent under this treatment (*Abstr.*, 1888, 798). If the bromine be removed from the bromohexylene by powdered caustic potash, intramolecular change need not, according to Faworsky, be feared; this method was, therefore, adopted, with the result that the *trimethylisoallylene* obtained agreed in properties with the hydrocarbon prepared by the action of alcoholic potash on the bromohexylene. The hydrocarbon is a clear, refractive liquid, having the usual odour of the hydrocarbons of the C_nH_{2n-2} series; it boils at 71—73°, and gives no precipitate with ammoniacal cuprous chloride or silver nitrate; its sp. gr. at 0°/0° is 0·7350. Evidence that the hydrocarbon is not methylisopropylacetylene was obtained by submitting it to the action of hypochlorous acid, when no α -dichloroketone was formed (compare Faworsky, *Abstr.*, 1895, i, 496). By brominating the hydrocarbon in the manner described at the beginning of this abstract, a hexylenic dibromide is obtained, which is probably



since it yields no glycol or unsaturated monobromide when heated with potassium carbonate. This dibromide is a colourless liquid, which boils at 78—79°, and has a sp. gr. at 0°/0° of 1·5878.

Methylisopropylacetylene was prepared from methyl isobutyl ketone by treatment with phosphorus pentachloride, and heating the product with alcoholic potash (compare Faworsky, *Abstr.*, 1888, 798). It boils at 71—72·5°; its sp. gr. at 0°/0° is 0·7321; it gives no precipitate with ammoniacal cuprous chloride or silver nitrate. When brominated, it takes up only one atom of bromine; the *monobromide* formed, either $CHMe_2\cdot CBr\cdot CHMe$ or $CHMe_2\cdot CH\cdot CMeBr$, is a clear liquid, boiling at 128—131°, and insoluble in water and in potassium carbonate solution.

The author hopes that this difference between the behaviour of trimethylisoallylene and methylisopropylacetylene towards bromine may prove to be a general one between trisubstituted isoallylenes and disubstituted isoallylenes; his present researches are in this direction.

A. G. B.

Mercuric Oxycyanide. By LEONCE BARTHE (*J. Pharm.*, 1896, [6], 182—184).—Dorvault's mercuric oxycyanide, $Hg(CN)_2\cdot HgO$, is

prepared by dissolving the yellow oxide (22 grams) in a solution consisting of mercuric cyanide (100 grams), and water (1500 grams); the temperature is not allowed to exceed 70° , and hydrogen cyanide is evolved. The oxycyanide requires more than 1000 parts of water to dissolve it, and the solution rapidly attacks nickel and steel. Ditte has described a second oxycyanide, $3\text{Hg}(\text{CN})_2, \text{HgO}$; it is practically identical with the pharmaceutical preparations which contain about 80.6 per cent. of mercuric cyanide; these readily dissolve in 200 parts of water, but nickel and steel articles placed in the solution become covered with mercury and mercuric oxide in less than 20 minutes, and hydrogen cyanide is evolved. Both these compounds are quite unsuitable for surgical purposes. J. B. T.

Synthesis of Ethylic Alcohol. By NIKODEMO CARO (*Chem. Centr.*, 1895, ii, 437; from *Chem. Ind.*, 1895, 226).—Ethyliidenic iodide is formed by passing acetylene, from calcium carbide through three Woulff's bottles containing concentrated hydriodic acid, it boils at 175° , "in a vacuum"; the yield is 55–57 per cent. When treated with potash, the iodide is converted into acetylene, and acetaldehyde, the latter is then further changed into alcohol (45 per cent.) and acetic acid. With moist silver oxide, acetylene is formed in traces only, but acetic acid is produced and the yield of alcohol is 90 per cent. When heated with water in a sealed tube at 130 – 150° , the iodide yields aldehyde, ethylic iodide, and hydriodic acid, but in presence of zinc oxide and zinc dust, alcohol is formed, the yield being 70 per cent. J. B. T.

Production of Alcohol from Cellulose and Wood. By E. SIMONSEN (*Bied. Centr.*, 1896, 25, 47–50; from *Norsk. teknisk. Tidsskr.*, 1895, 65–80).—The results of experiments on the production of sugar from sulphite cellulose showed that the best results are obtained when the following amounts of substances are employed: water 1080 c.c., cellulose 40 grams (or 27:1) with sulphuric acid 0.45–0.60 per cent. At a pressure of 8 or 6 atmospheres, the amount of sugar obtained was 45 per cent. of the weight of cellulose. Oxalic acid gave a much smaller yield than sulphuric acid. As regards the length of time of digestion, 20.1 per cent. of sugar was produced in 15 minutes, increasing to 42.7 per cent. with $1\frac{1}{2}$ hour, and diminishing to 35 per cent. after 3 hours' digestion. The introduction of chloroform, by means of which the high pressure was obtained at a lower temperature, caused a great reduction in the amount of sugar produced, indicating that temperature and not pressure is the more essential factor. Besides sugar, a considerable quantity of an acid substance is formed. The sugar seems to be *d*-glucose, but when fermented, yields about 20 per cent. less alcohol than is required by theory.

In the production of sugar from wood shavings (pine) the following conditions were found to give the best results (22.5 per cent.): digestion for $1\frac{1}{4}$ hour with 0.5 per cent. sulphuric acid, (5 parts) at a pressure of 9 atmos. With acid of over 1 per cent., much less sugar was obtained. In the case of wood, as with cellulose, an acid was produced along with the sugar, and the quantity of this

acid was greater the more sulphuric acid was employed; but the increased production of acid did not seem to take place at the expense of the sugar.

The lignin of the wood does not seem to be attacked, sugar being produced from the cellulose alone. The sugar, when fermented, yielded 64 per cent. of alcohol. Wood shavings yield 6.5 per cent. of alcohol.

N. H. J. M.

Bromo-Derivatives of Tricarbon Nuclei. By ROBERT LESPIEAU (*Bull. Soc. Chim.*, 1896, [3], 13, 629—632).—1:2:3-Tribromopropene, $\text{CHBr}:\text{CBr}:\text{CH}_2\text{Br}$, (Abstr., 1893, i, 1) is a colourless liquid, the vapour of which is irritating to the eyes. It boils at $89-90^\circ$ (10 mm.), and at $110-112^\circ$ (20 mm.), and is converted by potash into 1:3-dibromopropine, $\text{CBr}:\text{C}:\text{CH}_2\text{Br}$, a colourless liquid, having a very penetrating odour, and boiling at $52-55^\circ$ (15 mm.). 1:3:3-Tribromopropaneoxymethane, $\text{CH}_2\text{Br}:\text{CBr}_2:\text{CH}_2\cdot\text{OMe}$, obtained by brominating 2-bromopropeneoxymethane, $\text{CH}_2:\text{CBr}:\text{CH}_2\text{O}\cdot\text{Me}$, is a colourless liquid resembling camphor in odour; it boils at $118-119^\circ$ (35 mm.) and solidifies in a mixture of solid carbonic anhydride and ether; sp. gr. = 2.229 at 0° . 1:2-Dibromopropeneoxymethane, $\text{CHBr}:\text{CBr}:\text{CH}_2\cdot\text{OMe}$, obtained from the preceding compound by the action of sodium methoxide in methyl alcoholic solution, is a colourless liquid of ethereal odour; it boils at $175-177^\circ$ (745 mm.), and at the same time decomposes slightly; sp. gr. = 1.903 at 0° . It is converted by zinc dust in alcoholic solution into a propeneoxymethane, $\text{CH}:\text{C}:\text{CH}_2\cdot\text{OMe}$, but takes up bromine only very slowly, probably forming an additive compound. 1-bromopropeneoxymethane, $\text{CBr}:\text{C}:\text{CH}_2\cdot\text{OMe}$, is obtained by the regulated action of dry potash on dibromopropyleneoxymethane. It is a colourless, very volatile liquid, burning with a smoky flame, and boiling at 40° (20 mm.) or $125-126^\circ$ (740 mm.).

JN. W.

Isopropylic Hydrogen Sulphate. By LEOPOLD SPIEGEL (*Chem. Zeit.*, 1895, 19, 1423).—The acid obtained by Dobrin by acting on cardole with concentrated sulphuric acid, has the composition $\text{C}_3\text{H}_7\text{SO}_4\text{H}$; it is not identical with propylic hydrogen sulphate, and must therefore be isopropylic hydrogen sulphate. The latter compound, hitherto held to be incapable of existence, has been obtained by the author, in the form of its barium salt, by the following process.

Isopropylic alcohol is added gradually to sulphuric acid, both being ice cold, and the mixture poured into about 30 times its weight of ice-cold water. The solution is neutralised with barium carbonate, and the barium sulphate and excess of carbonate separated in the usual manner. Isopropylic barium sulphate, forms transparent crystals; it dissolves readily in water, and when heated at 85° , darkens and gives off the characteristic odour of the salt from cardole, barium sulphate being produced. The crystals on exposure to air become opaque, those of the normal propyl salt remaining transparent under the same conditions.

A. L.

Active Amyl Compounds. By IDA WELT (*Ann. Chim. Phys.*, 1895, [7], 6, 115—144).—The first portion of the paper contains

results which have already been published (compare Abstr., 1895, i, 203 and ii, 97).

Amylic phenylic ether, $C_5H_{11} \cdot OPh$, is obtained by heating dry sodium phenoxide with amylic iodide for about seven hours, it has a sp. gr. = 0.9331 at 17°, a specific rotatory power $[\alpha]_D = +4.01$ at 17°, and its molecular refraction = 51.55 (theory 51.13).

Amylic paratolylic ether, sp. gr. = 0.9408 at 17°, sp. rotatory power $[\alpha]_D = +4.26$ at 19°, and molecular refraction = 55.59 (theory 55.73).

Amylic orthotolylic ether, sp. gr. = 0.9839 at 20°, sp. rotatory power $[\alpha]_D + 3.86$ at 20°, and molecular refraction = 54.03.

Amylic metatolylic ether, sp. gr. = 0.9422 at 22°, sp. rotatory power $[\alpha]_D = +3.93$ at 22°, molecular refraction = 55.85.

Amylic thymylic ether, sp. gr. = 0.934 at 18°, sp. rotatory power $[\alpha]_D = +4.17$ at 18°, molecular refraction = 69.96 (theory 69.54).

Amylic carvacrylic ether, $C_5H_{11} \cdot O \cdot C_6H_3MePr$, sp. gr. = 0.955 at 19°, sp. rotatory power $[\alpha]_D = +4.0$ at 19°, and molecular refraction = 69.72.

From these and previous results, it follows that the amylic aromatic ethers have much higher rotatory powers than the amylic ethers of the fatty series. The author also points out that the oxides which contain a methyl group in the para-position relatively to the $O \cdot C_5H_{11}$ group have higher rotatory powers than the isomeric oxides which contain the methyl group in the ortho- or meta-position.

J. J. S.

Formation of Pinacolin from Calcium Isobutyrate. By CARL GLÜCKSMANN (*Monatsh.*, 1895, 16, 897—905).—The author has repeated the experiments of Barbaglia and Gucci (Abstr., 1881, 35), on the decomposition by heat of calcium isobutyrate, and has succeeded in isolating from the distillate a substance of the formula $C_6H_{12}O$; it is an oil, boiling at 114—116° (uncorr.); it has ketonic characters, dissolving in solutions of sodium hydrogen sulphite with development of heat. When oxidised with alkaline potassium permanganate, it yields oxalic and isobutyric acids, no appreciable amount of any ketonic substance being formed. It is, therefore, either methyl isobutyl ketone or ethyl isopropyl ketone, and not pinacolin.

Pinacolin may be detected with certainty, even when in small quantity, by means of the trimethylpyruvic acid, which it yields on oxidation. As the latter compound can not be detected in the oxidation products of the oils obtained in the above decomposition, the non-production of pinacolin during the latter is certain. A. L.

Properties of Dichlorhydrin. By HUGO FLEMMING (*Chem. Zeit.*, 1895, 19, 1550).—Dichlorhydrin destroys india-rubber and cork stoppers, and appears to have extraordinary solvent powers, dissolving all resins; thus amber dissolves in about 10 times its weight of the liquid, whilst copals seem to dissolve in all proportions, the solutions, however, cannot be filtered. This property is shown in a less degree by epichlorhydrin.

Pure dichlorhydrin boils at 176° under 765 mm. pressure, its sp. gr. = 1.364 at 15° .
A. L.

Multitrotation of Reducing Sugars and of Isodulcitol. By CHARLES TANRET (*Compt. rend.*, 1896, 122, 86—87).— β -Isodulcitol can be obtained in crystals in two ways: (a) 1 part of isodulcitol is dissolved in 0.5 part of water, and the warm solution is mixed with 5 parts of absolute alcohol and then with 9 parts of ether; α -isodulcitol is precipitated, but on adding more ether, the β -derivative is obtained in slender prismatic needles; (b) a solution of ordinary isodulcitol is concentrated on a water bath until it forms a thick syrup, and fragments of the β -compound obtained by the first process are added from time to time with constant agitation; β -isodulcitol separates as a crystalline anhydrous powder. The rotatory power of the product (a) is at first $[\alpha]_D = +10.29^{\circ}$, and of product (b) $+12^{\circ}$, but after an hour these numbers become $+9.6^{\circ}$ and $+10^{\circ}$ respectively.

The β -isodulcitol contains a third modification, γ -isodulcitol, which can be produced by heating at 90° the β -isodulcitol obtained by method (a). When first dissolved in water, its specific rotatory power is $+20^{\circ}$, but sinks to $+10^{\circ}$ after an hour.

Anhydrous isodulcitol softens at 105° , and melts distinctly at 108° ; when exposed to moist air, it combines with water and is partially reconverted into α -isodulcitol.
C. H. B.

Dichloralglucose and Chloralglucosan. By JEAN MEUNIER (*Compt. rend.*, 1896, 122, 142—144).—85 grams of chloral hydrate and 130 c.c. of sulphuric acid of 60° are triturated together, 100 grams of finely powdered glucose is added, and trituration continued. After a few minutes, the product is thrown into water, and the insoluble portion, after being well washed, is crystallised from boiling alcohol. It contains (1) chloralglucose, or chloralose, soluble in cold alcohol, and crystallising in needles which melt at 185 — 187° ; (2) dichloralglucose, $C_6H_{10}O_4(C_2Cl_3O)_2$, this crystallises in white needles, which melt at about 225° , dissolve in 300 parts of alcohol, and in 45 parts of ether at about 20° ; it is not decomposed by acids; (3) chloralglucosan, $C_6H_8O_4C_2Cl_3O$, which forms nacreous lamellæ, melting at about 225° , insoluble in water or in cold alcohol, but soluble in boiling alcohol. It requires 1,000 parts of ether for dissolution, and is not attacked by acids.

Dichloralglucose and chloralglucosan are reduced by zinc in presence of boiling acetic acid, and the products are under investigation.
C. H. B.

Hydrolysis and Estimation of Sugar. By JAMES O'SULLIVAN (*J. Soc. Chem. Ind.*, 1895, 14, 555—556).—The author has proved that a 10 per cent. solution of cane sugar, containing 4 per cent. of sulphuric acid by volume, was completely inverted at the ordinary temperature in about seven days.

The solution was then most carefully neutralised with barium carbonate and the copper-reducing power was taken. The result confirmed the generally accepted idea that the copper oxide, multiplied by 0.4535, represents the amount of invert sugar.
L. DE K.

Lintner's Isomaltose. By CHRISTOPH ULRICH (*Chem. Zeit.*, 1895, 19, 1523).—The author has repeated, under similar conditions, the work of Lintner and Düll (compare *Abstr.*, 1893, i, 5) on the action of diastase on starch. All the fractions of the product whose rotations approached that of Lintner's isomaltose, $[\alpha]_D = +140$, were mixed and refractionated as before, and the process repeated. From the final fractions, with the above specific rotation, osazones were prepared and fractionally crystallised, when they were found to melt most indefinitely, but in no case were they completely melted below 159° ; as a rule, they melted between 165° and 175° , whilst the osazone described by Lintner melted at 150 – 153° . The above osazone behaved, on recrystallisation, like maltosazone, and had nearly the same rotation; the author concludes that it is identical with that substance.

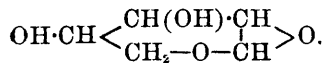
Crystals, deposited from various fractions of the syrup, were found in all cases to be maltose, whilst the accompanying syrup gave some quantity of glucosazone on treatment with phenylhydrazine.

From these results, the author concludes that the incomplete action of malt extract on starch at 70° , leads to the production, not of isomaltose, but of ordinary maltose (compare Ling and Baker, *Trans.*, 1895, 702, 739; Brown and Morris, *ibid.*, 709). A. L.

Ethereal Derivatives of Wood Gum [Xylan] and of Xylose.

By RICHARD BADER (*Chem. Zeit.*, 1895, 19, 55–56 and 78).—*Acetylxylan*, $C_5H_7AcO_4$, is obtained when finely powdered wood-gum, which has been air-dried, is treated with excess of acetic chloride. After warming for a few minutes on the water bath, the mixture is cooled, diluted with acetic acid, and then precipitated with an excess of absolute alcohol. The dry acetyl derivative forms a yellowish-brown, amorphous powder, which is but sparingly soluble in boiling acetic acid, and can only be further purified with great difficulty.

Diacetylxylan, $C_5H_6Ac_2O_4$, is formed when the monacetyl derivative is intimately mixed with a considerable excess of acetic anhydride and then heated in sealed tubes at 140 – 150° . It resembles the monacetyl compound in appearance, and is also very sparingly soluble in most solvents. The author has found it impossible to introduce more than two acetyl groups into the xylan molecule, a property which agrees with either of the two constitutions for xylan suggested by Tollens, namely, $CHO \cdot [CH \cdot OH]_2 \cdot CH < \begin{smallmatrix} O \\ | \\ CH_2 \end{smallmatrix}$, or



Benzoylxylan is best prepared by Baumann's method; after washing with water and boiling alcohol, it forms a brownish, amorphous mass, and is only sparingly soluble in boiling acetic acid. A dibenzoyl derivative could not be obtained.

A mixture of xylan *mono-* and *di-nitrate* is obtained when dried wood gum is added to cold nitric acid (sp. gr. 1.525), and the mixture is poured into cold water. The author has found it impossible to separate the two, and can find no trace of oxalic acid among the products of the action of concentrated nitric acid on xylan.

Stone's tetracetylxylose (Abstr., 1895, i, 104) may also be obtained by heating xylose with an excess of acetic anhydride for $2\frac{1}{2}$ —3 hours in a sealed tube at 140° . It forms small needles and melts at 126° (Stone, 123.5—124.5 $^{\circ}$). In attempting to prepare the tetracetyl compound, the author, on one occasion, obtained quite a different result. The product, when boiled with water, yielded a strong smell of turpentine oil, and, on distillation with superheated steam, a small quantity of a colourless oil passed over, and a brown resin was left. The quantities of these two products were too small for complete investigation, and the author could not obtain them in any subsequent experiment.

Pure xylose, when added to concentrated nitric acid (sp. gr. 1.48), yields no trace of oxalic acid, the anhydride of trihydroxyglutaric acid (probably the anhydride of Fischer's acid, compare Abstr., 1891, 177) apparently being formed. J. J. S.

Diastatic Resolution of Starch. By HANS MITTELMEIER (*Chem. Centr.*, 1895, ii, 163; from *Wchschr. Brauerei*, 12, 480—482).—Unlike Lintner, the author has failed to obtain maltose from its isomerides by the action of diastase. He regards the diastatic resolution of starch as occurring in two phases; in the first, a small portion of the starch is rapidly converted into amylo-, achroo-, and erythro-dextrins and sugar, but these dextrins are not identical with those formed later; the former are termed primary, the latter secondary, dextrins.

Primary erythrodestrin is deposited from water in an insoluble state, $[\alpha]_D =$ about $+170^{\circ}$; it is soluble in phenylhydrazine, reduces alkaline copper solution, and yields dextrose and maltose when treated with diastase. *Primary achroodestrin* has also been isolated. The sugar obtained from the primary dextrins yields, with phenylhydrazine, maltosazone; that from the secondary dextrins, an oily osazone, which softens at 120° , melts at 145 — 148° , and is probably derived from a new biose, for which the term *metamaltose* is suggested.

J. B. T.

Action of the Halogens on the Methylamines. By IRA REMSEN and JAMES F. NORRIS (*Amer. Chem. J.*, 1896, 18, 90—95).—When dry trimethylamine is passed into ice-cold bromine, it is absorbed, giving a yellow precipitate of *trimethylamine dibromide*, NMe_3Br_2 . The following method of preparation is more convenient. Trimethylamine hydrobromide (1 mol.), with just enough concentrated hydrobromic acid to dissolve it on heating, is mixed with bromine (1 mol.) and heated. On cooling, light yellow plates crystallise out, which, on recrystallisation from alcohol, are obtained as stout, prismatic needles. The salt is instantly decomposed by water, with liberation of just half the bromine. By passing trimethylamine into iodine dissolved in absolute alcohol, the *diiodide*, NMe_3I_2 , is obtained as a light yellow precipitate, which gradually changes to a dark brown, viscous liquid. Hydrochloric acid decomposes it immediately, with liberation of iodine, but water does not affect it until heated, when much more than half the iodine is set free, probably owing to the action of the hydriodic acid formed. The *dichloride* seems to be obtained by the action of dry chlorine on dry trimethyl-

amine. It is a white solid, is very hygroscopic, has a strong odour of chlorine, is very easily decomposed by moist air, and could not be analysed. With excess of chlorine, trimethylamine burns and deposits soot. The preparation and properties of *dimethylamine dibromide* are similar to those of the trimethylamine compound. Compounds containing two different halogen atoms were also obtained. Thus, the chloride of either di- or tri-methylamine gives with bromine a compound containing both bromine and chlorine, and the chlorides and bromides of both amines yield, with iodine, compounds which give up iodine in contact with water. Methylamine could not be made to yield either bromine or iodine substitution products by methods analogous to those described. A. E.

New Method of preparing Aliphatic Diazo-compounds. By WILHELM TRAUBE (*Ber.*, 1896, **29**, 667—670).—When the sodium or lead salt of an aliphatic isonitramic acid (*Abstr.*, 1895, i, 502) is reduced with sodium amalgam at 0°, the sodium salt of a diazo-acid is formed as the chief product of the action; some hydrazido-acid (compare this vol., i, 340) is also formed at the same time. Thus, sodium isonitramineacetate, $\text{HO}_2\text{N}_2\cdot\text{CH}_2\cdot\text{COONa}$, yields sodium diazoacetate, $\text{N}_2\cdot\text{CH}\cdot\text{COONa}$, and, by evaporating the resulting strongly alkaline solution at 30—40° under diminished pressure, this salt can be obtained as a yellow, crystalline substance, which explodes when heated, but not when struck; the yield is more than 50 per cent. of the theoretical. Neither the acid itself, nor its salts with heavy metals, are stable; they decompose at once in aqueous solution with evolution of nitrogen.

In the case of the homologues, it was not possible to isolate salts of the diazo-acids; solutions, however, were obtained which evolved nitrogen when acidified, and doubtless contained such salts.

C. F. B.

Hydrazine, Azoimide, and Aliphatic Diazo-derivatives. By THEODOR CURTIUS (*Ber.*, 1896, **29**, 759—783).—A lecture delivered to the German Chemical Society. The discovery of ethylic amidoacetate hydrochloride rendered it necessary to show that the ethylic group was linked to carboxyl, and not to nitrogen; proof of this is afforded by the action of nitrous acid, which results in the formation of ethylic diazoacetate; the synthesis of methyleneamidoacetonitrile, $\text{CH}_2\text{N}\cdot\text{CH}_2\cdot\text{CN}$, from formaldehyde and ammonium cyanide, and its conversion into formaldehyde and amidoacetic acid, rendered the latter compound easily accessible. Etheral salts of diazo-acids may be prepared directly from albuminous matter, such as glue, cheese, or old woollen fibres, by the successive action of alcoholic hydrogen chloride and sodium nitrite, and they may be immediately converted into hydrazine; in this manner, it is possible, in the course of a few minutes, to demonstrate the presence of amido-groups in egg-albumin. Diazoacetic acid is only known in the form of its amide, alkali, and etheral salts, but the ethylic salt forms salts with the heavy metals; when heated, it yields ethylic azinesuccinate, $\text{N}_2\left(\begin{array}{c} \text{CH}\cdot\text{COOEt} \\ | \\ \text{CH}\cdot\text{COOEt} \end{array}\right)_2$, which readily decomposes, on further heating, into nitrogen and

fumaric acid. Ethylic diazosuccinate yields an isomeric azinesuccinate, probably the asymmetric compound $N_2[C(COOEt) \cdot CH_2 \cdot COOEt]_2$; neither of these azines give hydrazine when hydrolysed.

Diazoacetic acid, like diazomethane, reacts with almost all substances, including organic and mineral acids, haloids, water, alcohols, phenols, hydrocarbons, aniline, and benzaldehyde; in all these cases, nitrogen is replaced by hydrogen and a radicle: thus, with water and alcohol, respectively, glycollic acid and ethylglycollic acid are formed. With dilute alkali, ethylic diazoacetate yields the normal salt, which, when acidified, is converted into glycollic acid, but, with concentrated alkali, triazoacetic acid, $COOH \cdot CH < \begin{smallmatrix} N_2 \cdot CH(COOH) \\ N_2 \cdot CH(COOH) \end{smallmatrix} > N_2$, is formed, and this, when hydrolysed by means of dilute mineral acids, is converted into hydrazine and oxalic acid, or carbonic anhydride and formic acid; hydrazine is also formed by the reduction of azoacetic acid to hydrazineacetic acid, $COOH \cdot C < \begin{smallmatrix} NH \\ NH \end{smallmatrix}$, and the hydrolysis of

this to glyoxalic acid; von Pechmann's synthesis of it from diazoacetic acid and alkali sulphite, and Buchner's from ethylic diazoacetate and salts of unsaturated acids, such as ethylic fumarate, are analogous. Thiele's method, which is of much practical importance, consists in reducing nitroguanidine prepared from potassium ferrocyanide, to amidoguanidine, which is then hydrolysed to hydrazine, carbonic anhydride, and ammonia.

Hydrazine is characterised by its powerful reducing action, many salts which yield the lower oxides with other reducing agents are converted into metals by hydrazine; the haloids and sulphur are converted into hydrogen compounds, and zinc slowly dissolves, forming a crystalline salt. Although hydrazine is apparently symmetrical, its derivatives

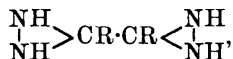
of the type $N_2H_6'' = \overset{v}{NH_3} \cdot \overset{v}{NH_3}$, such as $N_2H_4 \cdot 2H_2O$ and $N_2H_4 \cdot 2HCl$, are highly unstable, whilst those of the type $N_2H_5 = \overset{v}{NH_2} \cdot \overset{v}{NH_3}$, such as $N_2H_4 \cdot HCl$ and $N_2H_4 \cdot H_2O$, are stable; the sulphate is an exception, it does not form an alum, but yields anhydrous double salts, $(N_2H_5)_2SO_4 \cdot R''SO_4$ ($R'' = Cu, Ni, Co, Fe, Mn, Cd, Zn$, but not Mg), but the double chlorides $N_2H_5Cl \cdot R''Cl_2$ and $(N_2H_5Cl)_2 \cdot R''Cl_2$ correspond with the ammonium derivatives; thus, the compound $NiSO_4 \cdot 6NH_3$ has its analogue in $NiSO_4 \cdot 3N_2H_4$, which, like nickel carbonyl, indicates the possible octovalency of nickel.

Azoimide is formed from nitrous anhydride and hydrazine; Thiele obtained it from amidoguanidine in a similar manner, and Wislicenus from nitrous oxide and ammonia in presence of sodium. The author's method consists in converting an insoluble amide into a hydrazide, $R \cdot CO \cdot NH \cdot NH_2$, which is then transformed, by means of nitrous acid, into the azoimide $RCON_3$; this, when hydrolysed with alcoholic ammonia, regenerates the amide and forms ammonium azoimide, which may be employed with perfect safety. Azoimide itself was only obtained anhydrous on one occasion; it has a powerful smell, and boils at about the same temperature as ether; subsequent attempts to isolate it were unsuccessful, as it always exploded with great violence

at the ordinary temperature. The ammonium salt is employed as an explosive, but with care it may be sublimed like ammonium chloride. The hydrazine salt, $N_2H_5N_3$, forms large, hygroscopic crystals, which burn quietly, like gun-cotton. In general chemical behaviour, the group N_3 resembles a haloid atom. Hydrazine hydrate reacts with ethylic iodide, like potash, giving ethylene and hydrazine iodide; its constitution is shown by the production of 1 : 2 : 4-dinitrophenyl-hydrazine from 1 : 2 : 4-dinitraniline and from 1 : 2 : 4-dinitrobromobenzene.

The aldehyde hydrazones are unsymmetrical, $R \cdot CHN \cdot NH_2$, and are readily converted into azines, $RCH \cdot N \cdot N \cdot CHR$, which, when reduced, yield hydrazines, analogous to hydrazobenzene, but these do not yield azo-derivatives, $R \cdot CH_2 \cdot N \cdot N \cdot CH_2R$, by oxidation. The ketohydrazones and azines resemble the aldehyde derivatives, and, if the ketazines contain the group $-CMe \cdot N-$, they readily yield pyrazoline derivatives, pyrazoline itself being spontaneously formed from acrylhydrazoue, $CH_2 \cdot CH \cdot CH \cdot N \cdot NH_2 = NH < \begin{smallmatrix} CH_2 \cdot CH_2 \\ N = CH \end{smallmatrix}$. By the action of bromine, pyrazoline yields pyrazole, $NH < \begin{smallmatrix} CH \cdot CH \\ N = CH \end{smallmatrix}$.

Orthoketones and ethereal salts of α -ketonic acids react with hydrazine to form hydrazi-derivatives, $R \cdot CO \cdot CR < \begin{smallmatrix} NH \\ NH \end{smallmatrix}$ or



which, on oxidation, yield azo-compounds, whilst the hydrazones give unstable tetrazones, then ketazines and nitrogen; the hydrazi-derivatives do not form ketazines when heated, but nitrogen is eliminated; thus, hydrazibenzil is converted into deoxybenzoin. Ethereal salts of β - and γ -ketonic acids react with hydrazine as with phenylhydrazine, except that the resulting compounds usually change spontaneously into derivatives of pyrazolone and pyridazinone. von Rothenburg's synthesis of pyrazolone from hydrazine and ethylic propiolate, and of pyrazolidone from hydrazine and acrylic acid, are referred to,

also the compound, $C_6H_4 < \begin{smallmatrix} CO \cdot NH \\ CO \cdot NH \end{smallmatrix}$, from phthalic anhydride. Hydr-

azine reacts with ethereal salts to form acid hydrazides, $R \cdot CO \cdot NH \cdot NH_2$. Amides, acid chlorides, and azoimides react like the ethereal salts; by the action of iodine, or of a second molecule of the ethereal salt, the hydrazides are converted into symmetrical secondary hydrazines, $R \cdot CO \cdot NH \cdot NH \cdot COR$; the hydrazides condense with aldehydes, forming tertiary hydrazines, $RCO \cdot NH \cdot N \cdot CHR$, which are entirely different from the aldazines (see above). With nitrous acid, the hydrazides are converted into azoimides, $R \cdot CON_3$ (see above), which closely resemble the acid chlorides and bromides, except that those of the aliphatic series are explosive; with diazo-salts, the same change takes place, but buzylene derivatives are formed as intermediate compounds: thus, benzhydrazide and diazobenzene yield phenylbenzoylbuzylene, $COPh \cdot NH \cdot NH \cdot N \cdot NPh$; this, according to circumstances, gives benz-

azoimide, $\text{Ph}\cdot\text{CON}_3$, and aniline, or benzamide and phenylazoimide, PhN_3 . The azoimides are converted, by the action of water, into nitrogen, carbonic anhydride, and carbamide derivatives; alcohol acts in a similar manner, but yields urethanes instead of carbonic anhydride and carbamides. These reactions furnish a ready means of replacing carboxyl by the amido-group, the steps being, acid—ethylic salt—hydrazide—azoimide—urethane—amine. The hydrazides and azoimides react to form semicarbazides, and nitrogen derivatives of "prozane," $\text{NH}_2\cdot\text{NH}\cdot\text{NH}_2$, are not formed, as might have been expected. The azoimide and hydrazide derivatives of carbonic acid are of special interest; they include semicarbazide, $\text{NH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{NH}_2$, dicarbamide, $\text{CO}<\text{NH}\cdot\text{NH}>\text{CO}$, an energetic acid, and carbazoimide, CON_6 , which is highly explosive.

J. B. T.

Hydrazido-acids. By WILHELM TRAUBE and G. G. LONGINESCU (*Ber.*, 1896, **29**, 670—675).—When an isonitramic acid is reduced with sodium amalgam at 0° (compare this vol., i, 337), there is formed, in addition to the salt of the diazo-acid, a hydrazido-acid, in amount equal to about 5 per cent. of that theoretically possible. Thus, isonitraminepropionic acid, $\text{HO}_2\text{N}_2\cdot\text{CHMe}\cdot\text{COOH}$, yields hydrazidopropionic acid, $\text{NH}_2\cdot\text{NH}\cdot\text{CHMe}\cdot\text{COOH}$. This acid is isolated by acidifying the solution, when the diazo-acid is destroyed, and then forming the benzylidene derivative of the hydrazido-acid by adding benzaldehyde until the solution no longer reduces Fehling's solution. This derivative sometimes separates out in crystals, but usually has to be extracted with ether; it is readily decomposed by steam distillation, or by warming with dilute acid, into benzaldehyde and the hydrazido-acid, the latter being obtained when the residue is evaporated. These hydrazido-acids reduce Fehling's solution, and form salts with acids, but not with bases.

Hydrazidoacetic acid could not be isolated. *Hydrazidopropionic acid* melts at 180° , its *benzylidene derivative* at 106° , its *hydrochloride* at 155° . It condenses with ethylic acetoacetate, forming crystals which lose yet a molecule of alcohol when evaporated with water, and form methylpyrazolonepropionic acid, melting at 215° . *Hydrazidobutyric acid* melts at 208° , its *benzylidene derivative* at 125° ; *hydrazidovaleric acid* at 215° , its *benzylidene derivative* at 116° ; *hydrazidobenzylacetic acid* at 196° , its *benzylidene* and *salicylidene derivatives* at 153° and 134° respectively.

C. F. B.

Hydrazine Derivatives of Isobutyric acid. By JOHANNES THIELE and KARL HEUSER (*Annalen*, 1896, **290**, 1—43).—The authors' improvement in the preparation of semicarbazide (this vol., i, 208) has enabled them to investigate the hydrazine derivatives of isobutyric acid.

Benzylidenehydrazidoisobutyric acid, $\text{CHPh}\cdot\text{N}\cdot\text{NH}\cdot\text{CMe}_2\cdot\text{COOH}$, is obtained by hydrolysing carbonamidohydrazoisobutyronitrile, which Thiele and Stange obtained from acetonesemicarbazone by the action of hydrogen cyanide (*Abstr.*, 1895, i, 252), and treating the product

with benzaldehyde; it is insoluble in water, and crystallises from alcohol in white needles melting at 144—145°. The *silver* salt dissolves with difficulty, and rapidly becomes black.

Hydrazidoisobutyric acid, $\text{NH}_2\cdot\text{NH}\cdot\text{CMe}_2\cdot\text{COOH}$, is formed from the preceding compound on submitting it to the influence of a powerful current of steam; it dissolves readily in water, but is insoluble in alcohol or ether, and melts and decomposes at 237°. The acid reduces cold Fehling's solution and an ammoniacal silver solution, and yields hydrazine when treated with boiling acids, although caustic soda does not produce this effect; bromine water and ferric chloride oxidise the substance, the former agent liberating the quantitative amount of nitrogen, along with carbonic anhydride. The *hydrochloride* crystallises from water in rosettes of needles, and melts at 156—157°, the *sulphate* melts and decomposes at 189°, and the *nitrate* crystallises in leaflets and melts at 146°; the *ethylic* salt boils at 93—95° under a pressure of 13 mm., and yields a crystalline *hydrochloride*.

3-Methylpyrazoloneisobutyric acid, $\text{COOH}\cdot\text{CMe}_2\cdot\text{N} < \begin{smallmatrix} \text{N}=\text{CMe} \\ \text{CO}\cdot\text{CH}_2 \end{smallmatrix}$, is obtained by agitating a concentrated aqueous solution of hydrazidoisobutyric acid with ethylic acetoacetate; it crystallises from hot water in yellowish needles, and melts at 263°. A red coloration is developed with ferric chloride.

The *mononitrile* of hydrazodiisobutyric acid (*hydrazoisobutyronitrilic acid*), $\text{COOH}\cdot\text{CMe}_2\cdot\text{NH}\cdot\text{NH}\cdot\text{CMe}_2\cdot\text{CN}$, is formed when concentrated aqueous solutions of hydrazidoisobutyric acid and potassium cyanide are agitated with acetone (1 mol.), and after 24 hours treated with the calculated quantity of hydrochloric acid; it melts at 100°, is readily soluble in alcohol and ether, dissolves sparingly in petroleum, and reduces ammoniacal silver and Fehling's solution.

The *dinitrile*, $\text{CN}\cdot\text{CMe}_2\cdot\text{NH}\cdot\text{NH}\cdot\text{CMe}_2\cdot\text{CN}$, is obtained by agitating hydrazine sulphate and potassium cyanide (2 mols.) in concentrated aqueous solution with acetone (2 mols.); it crystallises from ether in lustrous plates, and melts at 92—93°. The *hydrochloride* is amorphous, and loses hydrogen chloride when exposed to air; the *dinitroso*-derivative melts at 43—44°, and yields azo-isobutyronitrile (see below) when heated or exposed to air, nitric oxide being eliminated.

Hydrazodiisobutyric acid, $\text{COOH}\cdot\text{CMe}_2\cdot\text{NH}\cdot\text{NH}\cdot\text{CMe}_2\cdot\text{COOH}$, which is formed on hydrolysing the dinitrile with concentrated hydrochloric acid, crystallises from water in lustrous prisms, melting at 223—224°; the aqueous solution is acidic, and the substance, although a dicarboxylic acid, is monobasic in character. The *ammonium* salt is a lustrous, crystalline powder, and the *silver* salt rapidly becomes black; the *calcium* salt crystallises in needles, and contains 2H₂O, the *potassium* salt is crystalline, and the *hydrochloride*, which contains 1H₂O, separates in aggregates of small needles. The *methylic* salt separates from petroleum in long, lustrous prisms, melts at 53—54°, and boils at 216°; the *ethylic* salt boils at 231—233°, and has the sp. gr. = 0.99784 at 23°/4°. When hydrazodiisobutyric acid is heated at 200° in a vacuum, it sublimes in crystals which melt at 223—224°, but, under atmospheric pressure, ammonia and carbonic anhydride are evolved, along with inflammable gas which reduces an ammo-

niacal silver solution; in a sealed tube at 270° , the acid gives rise to a crystalline compound which has the formula $C_8H_{14}N_2O_2$, and does not melt at 250° .

Azodiisobutyronitrile, $CH \cdot CMe_2 \cdot N:N \cdot CMe_2 \cdot CN$, is produced on oxidising hydrazodiisobutyronitrile with bromine water, and crystallises from ether in long, silvery prisms, which melt and evolve gas at $105-106^{\circ}$; on the application of heat, the whole of the azoic nitrogen is liberated quantitatively. The *hydrochloride* of azodiisobutyric acid imidomethyl ether, $N_2[CMe_2 \cdot C(OEt):NH, HCl]_2$, is formed when hydrogen chloride acts on azodiisobutyronitrile suspended in methylic alcohol; it melts and decomposes at $133-134^{\circ}$, and loses hydrogen chloride when treated with water. The *hydrochloride* of azodiisobutyric acid imidoethyl ether melts at $106-107^{\circ}$, yielding nitrogen and methylic chloride; the clear, aqueous solution becomes turbid when heated, yielding the ethylic salt of azodiisobutyric acid (see below), and this substance, on the application of heat, yields white prisms which melt at 124° , and probably consist of tetramethylsuccinamide. The *amidoxime* of azodiisobutyric acid, $NH_2 \cdot C(NO_2) \cdot CMe_2 \cdot N:N \cdot CMe_2 \cdot C(NO_2) \cdot NH_2$, is obtained by the action of hydroxylamine on azodiisobutyronitrile; it melts at 154° .

Ethylic azodiisobutyrate, $COOEt \cdot CMe_2 \cdot N:N \cdot CMe_2 \cdot COOEt$, is formed by the oxidation of ethylic hydrazodiisobutyrate with bromine water in presence of dilute hydrochloric acid; the yellowish liquid, which has the sp. gr. = 0.9884 at $24.6^{\circ}/4^{\circ}$, loses its nitrogen quantitatively at 95° . Stannous chloride reduces the salt to ethylic hydrazodiisobutyrate. *Methylic azodiisobutyrate* is obtained by oxidising methylic hydrazodiisobutyrate; it crystallises from light petroleum in large plates, and melts at 33° , nitrogen being eliminated quantitatively above 80° . The *amide* of azodiisobutyric acid is produced by the action of ammonia on the foregoing salts, and crystallises from dilute alcohol in rhombic plates, which melt and decompose at $94-95^{\circ}$; it contains $2H_2O$, which is lost in the exsiccator. The amide crystallises from methylic alcohol in anhydrous plates, and in this condition melts at 104° ; when suspended in hot olive oil, the azoic nitrogen is eliminated quantitatively. *Potassium azodiisobutyrate* contains $1H_2O$, softens at 180° , and melts and decomposes at 250° ; it is obtained from the methylic and ethylic salts by the action of potash dissolved in methylic alcohol. An aqueous solution of this salt is strongly alkaline, and slowly reduces ammoniacal silver solution when heated; acids induce effervescence, liberating carbonic anhydride, the acetone compound of hydrazidoisobutyric acid being formed at the same time.

Tetramethylsuccinonitrile, $CN \cdot CMe_2 \cdot CMe_2 \cdot CN$, is obtained by treating azodiisobutyronitrile with water heated almost at 100° , nitrogen being eliminated; it crystallises from very dilute alcohol in lustrous, silvery leaflets and prisms, and melts at 169° . When hydrolysed with 80 per cent. sulphuric acid, it yields a mixture of tetramethylsuccinic acid and its anhydride. *Ethylic tetramethylsuccinate*, is formed when ethylic azodiisobutyrate is heated on the water bath; it boils at $218-220^{\circ}$.

M. O. F.

Semicarbazones. By MAX SCHOLTZ (*Ber.*, 1896, **29**, 610—613).—When the semicarbazones, $\text{CRR}'\text{N}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2$, of dimethyl ketone, methyl ethyl ketone, or methyl propyl ketone (the last named melts at 100°) are distilled alone, they yield bis-azimethylenes, $\text{N}_2(\text{CRR}')_2$, and hydrazodicarbonamide, $\text{N}_2\text{H}_2(\text{CO}\cdot\text{NH}_2)_2$, the latter decomposing for the most part into the imide and ammonia.

Mesityl oxide semicarbazone melts at 156° ; when distilled, it does not decompose, but is converted into an isomeride which melts at 129° and boils at $212-213^\circ$; simple melting is even sufficient to effect the transformation. C. F. B.

Inorganic Derivatives of Secondary Aliphatic Amines. By C. A. AUGUST MICHAELIS and K. LUXEMBOURG (*Ber.*, 1896, **29**, 710—715).—*Chlorophosphines*, $\text{NR}_2\cdot\text{PCl}_2$, are obtained on slowly adding the amine (2 mols.) to phosphorous chloride (1 mol.), cooling meanwhile; they are slowly decomposed by water. *Diethylaminechlorophosphine* boils at 189° under atmospheric, and at $72-75^\circ$ under 14 mm. pressure; its sp. gr. = 1.196 at 15° ; *diisobutylaminechlorophosphine* melts at $37-38^\circ$, and boils at $115-117^\circ$ under 16 mm. pressure; *piperidinechlorophosphine* boils at $94-95^\circ$ under 10 mm. pressure.

Oxychlorophosphines, $\text{NR}_2\cdot\text{POCl}_2$, are obtained by adding an ethereal solution of phosphorus oxychloride to a cooled ethereal solution of the amine (2 mols.); they smell either like camphor or like pepper, are only very slowly decomposed by water, and yield ethereal salts with sodium ethoxide or phenoxide, hydrazides with phenylhydrazine, and tertiary phosphine oxides with aromatic amines. *Diethylamineoxychlorophosphine* boils at 100° under 15 mm. pressure; *dipropylamineoxychlorophosphine* boils at 170° under 80 mm. pressure, and its sp. gr. = 1.1799 at 13° , and index of refraction = 1.4653; *diisobutylamineoxychlorophosphine* melts at 54° , and can be distilled under diminished pressure; *diamylamineoxychlorophosphine* boils at 150° under 12 mm. pressure, and its sp. gr. = 1.0804 at 13° .

Thiochlorophosphines, $\text{NR}_2\cdot\text{PSCl}_2$, are obtained by heating a mixture of the amine (2 mols.) with phosphorus thiosulphochloride (1 mol.) at $100-120^\circ$; they are very stable substances, smell like camphor, and react like the oxychlorophosphines. *Diethylaminethiochlorophosphine* boils at 100° under 15 mm. pressure, and its sp. gr. = 1.105 at 15° ; *dipropylaminethiochlorophosphine* boils at $132-134^\circ$ under 15 mm. pressure, and its sp. gr. = 1.077 at 15° ; *diisobutylaminethiochlorophosphine* melts at 36° , and boils at 150° under 10 mm. pressure; *diamylaminethiochlorophosphine* boils at $160-163^\circ$ under 10 mm. pressure, and its sp. gr. = 1.0288 at 15° .

Chlorarsines, $\text{NR}_2\cdot\text{AsCl}_2$, can be obtained in the same way as the chlorophosphines. *Diisobutylaminechlorarsine* is crystalline, and boils at 125° under 15 mm. pressure.

Chlorosilicines, $\text{NR}_2\cdot\text{SiCl}_2$, are obtained by the action of the amine (2 mols.) on silicon chloride (1 mol.); they fume in the air, and are slowly decomposed by water. *Diethylaminechlorosilicine* boils at 104° under 80 mm. pressure; *diisobutylaminechlorosilicine* at $120-124^\circ$ under 30 mm. pressure.

Chloroborines, $\text{NR}_2\cdot\text{BCl}_2$, are obtained by treating boron chloride

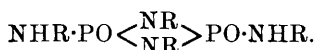
with the amine, cooling meanwhile; they colour the Bunsen flame a vivid green, fume in the air, and are at once decomposed by water. *Diethylaminechloroborine* boils at 140—144° under atmospheric pressure; *dipropylaminechloroborine* at 99° under 45 mm. pressure; and *diisobutylaminechloroborine* at 92—95° under 17 mm. pressure.

In addition to these, compounds such as $\text{NR}_2\cdot\text{Cl}$, $\text{NR}_2\cdot\text{OH}$, &c., are known, so that the imido-hydrogen atom of secondary aliphatic amines can be replaced by atoms belonging to very different groups of the periodic system.

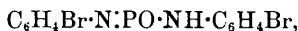
C. F. B.

Oxyphosphazo-compounds. By C. A. AUGUST MICHAELIS and E. SILBERSTEIN (*Ber.*, 1896, **29**, 716—728).—Oxyphosphazo-compounds, $\text{NR}\cdot\text{PO}\cdot\text{NHR}$, are most conveniently prepared by heating a primary aromatic amine (2 mols.) and phosphorus oxychloride (1 mol.) with enough xylene to make the mass into a paste; they can also be obtained by heating either secondary oxychlorophosphines, $(\text{NHR})_2\text{POCl}$, or tertiary phosphine oxides, $(\text{NHR})_2\text{PO}$. They are white, sandy powders, occasionally in small crystals, melt at a high temperature, and are insoluble, or only slightly soluble, in the ordinary solvents; from the chemical point of view, they are extremely stable. In analysing them, the carbon had to be determined by oxidation in the wet way; the ordinary method yielded results which were too low. They dissolve in alcoholic sodium ethoxide, or phenol, forming ethyl and phenyl derivatives, probably with the constitution $(\text{NHR})_2\text{PO}\cdot\text{NR}\cdot\text{PO}(\text{OEt})\cdot\text{NHR}$ (the phenyl compound in some cases has the constitution $\text{OPh}\cdot\text{PO}\cdot(\text{NHR})_2$).

In the case of oxyphosphazobenzeneanilide, which was studied in greater detail, the further action of phenol at a higher temperature results in the formation of the phenylic salt, $\text{NHPh}\cdot\text{PO}(\text{OPh})_2$. Heating for six hours with water, alcohol, or dilute aqueous soda, at 150° effects a decomposition into aniline, orthophosphoric acid, and *trianilinephosphine hydroxide*, $(\text{NHPh})_3\text{P}(\text{OH})_2$, which melts at 217°. Heating with concentrated sulphuric acid, or with hydrochloric acid in a sealed tube, decomposes it into aniline and phosphoric acid; and on prolonged heating with glacial acetic acid, it yields aniline, orthophosphoric acid, and *trianilinephosphine oxide*, $(\text{NHPh})_3\text{PO}$, the last being also formed when the phosphazo-compound is heated with aniline at a moderate temperature. It is suggested that these oxyphosphazoanilides have in reality double the formula given above, and that their structure is represented by the formula



The following is a list of the compounds described, with their melting points:—*Oxyphosphazobenzeneanilide*, $\text{NPh}\cdot\text{PO}\cdot\text{NHPh}$, 357°; *ethylic salt*, 220°; *phenylic salt*, 240°. [A crystallised compound, $(\text{NHPh})_3\text{PO} + \text{NH}_2\text{Ph}$, was incidentally prepared; it melts at 280°.] *Oxyphosphazometachlorobenzenechloranilide*, $\text{C}_6\text{H}_4\text{Cl}\cdot\text{N}\cdot\text{PO}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\text{Cl}$, 341°. *Oxyphosphazometabromobenzenebromanilide*,



329°; *ethylic salt*, 203°; forms, with aniline, a compound,



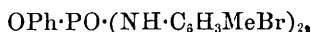
165°. The *oxyphosphazo-compounds* of *dichlor-* [$\text{NH}_2 : \text{Cl}_2 = 1 : 2 : 4$], *dibrom-* (335°), *trichlor-* (285°), and *tribrom-aniline* were also prepared; the first of these yields, with phenol, a compound,



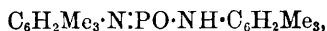
melting at 227°, and decomposed by boiling water. *Oxyphosphazoparatoluenetoluidide*, $\text{C}_6\text{H}_4\text{Me}\cdot\text{N}\cdot\text{PO}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\text{Me}$, 328°; *bromoparatoluidine* [$\text{Me} : \text{Br} : \text{NH}_2 = 1 : 3 : 4$] yields an analogous derivative which is converted by hot acetic acid into the compound



melting at 268°, and by phenol into the compound



melting at 221°. *Oxyphosphazoothotoluenetoluidide*, 309°. *Oxyphosphazo-compounds* of *mesidine* and *pseudocumidine*,



were also prepared; they melt at 240° and 217° respectively.

C. F. B.

Production of Gaseous Formaldehyde. By ANDRÉ BROCHET (*Compt. rend.*, 1896, **122**, 201—203).—The incomplete combustion of methylic alcohol yields only a small quantity of formaldehyde, accompanied by a large quantity of water and a notable proportion of carbonic oxide. The preparation of the gaseous aldehyde for purposes of disinfection is best accomplished by passing a current of hot gas over coarsely powdered trioxymethylene. The dilution of the aldehyde prevents repolymerisation, and the absence of water vapour makes it possible to apply the method to the disinfection of books, papers, and other articles that would be injured by moisture.

C. H. B.

Aldehydes derived from the Isomeric Alcohols $\text{C}_{10}\text{H}_{18}\text{O}$. By PHILIPPE BARBIER and LOUIS BOUVEAULT (*Compt. rend.*, 1896, **122**, 84—86).—The aldehydes obtained by the oxidation of licareol, licarhodol and geraniol (lemonol) were converted into semicarbazones (this vol., i, 311), and yielded the compounds previously described in approximately the same proportions. It follows that all three aldehydes are mixtures of the same compounds. The aldehyde of licareol was not obtained, because the sulphuric acid converts the licareol into licarhodol, $\text{CH}_2\cdot\text{CMe}\cdot\text{C}(\text{CH}_2\cdot\text{OH})\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CMe}\cdot\text{CH}_2$, becoming $\text{CH}_2\cdot\text{CMe}\cdot\text{CH}(\text{CH}_2\cdot\text{OH})\cdot\text{CH}_2\cdot\text{CH}\cdot\text{CMe}_2$. On the other hand, licarhodolaldehyde in presence of sulphuric acid is largely converted into lemonaldehyde, and the change is not reversible;



becomes $\text{CMe}_2\cdot\text{C}(\text{CHO})\cdot\text{CH}_2\cdot\text{CH}\cdot\text{CMe}_2$.

The aldehyde in oil of lemon consists mainly of lemonaldehyde, with small quantities of licarhodaldehyde. C. H. B.

Preparation of Glyoxal. By LEOPOLD SPIEGEL (*Chem. Zeit.*, 1895, **19**, 1423).—In preparing glyoxal by Ljubawin's method (compare Abstr., 1878, 23), much labour may be saved, and the yield of substance increased if the oxidation is at first carried out in a freezing mixture, and the temperature allowed gradually to rise to 25°; if now the acetic acid is distilled off under a pressure of 25–30 mm., the formation of oxalic acid may be entirely avoided, and the brittle, colourless, somewhat gummy, residual mass has all the properties of pure glyoxal. A somewhat better yield is obtained if, before distillation, the oxidation mixture is allowed to remain until all odour of aldehyde has disappeared. A. L.

Preparation of Acid Fluorides. By ALBERT COLSON (*Compt. rend.*, 1896, **122**, 243–244).—Acid fluorides can be prepared in the same manner as acid chlorides and bromides (this vol., i, 282). When acetic anhydride is saturated with dry hydrogen fluoride, acetic fluoride is formed, with very great development of heat. It boils at 20·8° under a pressure of 770 mm.; sp. gr. = 1·0369 at 0°. *Propionic fluoride*, obtained in a similar way, boils at 43·5° under a pressure of 765 mm.; sp. gr. = 0·974 at 10°; vapour density normal. It is slowly attacked by water, but rapidly by solutions of alkalis.

Instead of passing hydrogen into the acid anhydrides, a mixture of the anhydride and sulphuric acid may be allowed to act on sodium hydrofluoride, NaHF₂. C. H. B.

Acid Fluorides. By MAURICE MESLANS and F. GIRARDET (*Compt. rend.*, 1896, **122**, 239–242).—Acid chlorides act on many metallic fluorides, but the acid fluorides are best obtained by the action of the corresponding chlorides on dry zinc fluoride. The action takes place without extraneous heating, and the yield is almost quantitative.

Propionic fluoride is a colourless, very mobile liquid, which boils at 44°; sp. gr. = 0·972 at 15°. *Benzoic fluoride* has a very irritating odour, and boils at 154°. Both fluorides attack glass rapidly in presence of traces of moisture, but are only slightly soluble in, and slowly decomposed by, water. They are, however, rapidly attacked by solutions of alkalis, react slowly with alcohols to form ethers, and rapidly with ammonia, forming amides. C. H. B.

The Composition of Wool-fat. By L. DARMSTAEDTER and ISAAC LIFSCHÜTZ (*Ber.*, 1896, **29**, 618–622; compare this vol., i, 198).—The fractions previously obtained by the neutralisation of the alcohols of wool-fat have been further examined, and have been found to consist of the potash salts of myristic acid and carnaubic acid (Stürcke, Abstr., 1884, 1280). These two acids make up about 10–12 per cent. of the whole mass. A. H.

Cerotic acid and Melissic acid, the Free acids of Beeswax. By THEOD. MARIE (*J. Pharm.*, 1896, [6], **3**, 107–111; compare Abstr.,

1895, i, 81).—Cerotic acid melts at 77.9° (corr.). The crystals deposited from alcohol vary according to the purity of the acid; if it contains neutral substances, it forms a gelatinous mass consisting of microscopic needles, and containing a large proportion of alcohol; if melissic acid is present, short, granular crystals are rapidly deposited. Pure cerotic acid crystallises in stellate, microscopic needles; from benzene, it separates in dense laminæ; from ether, it is deposited in tabular masses consisting of large, aggregated needles. The methylic salt is deposited in pearly needles melting at 62.5° . Nafzger's compound (m. p. 60°) was probably a mixture of methylic cerotate and methylic melissate. Its solubility resembles that of the acid. The ethylic salt is less lustrous, and more readily soluble in ether than the preceding compound, and melts at 60.5° . The *barium salt*, $(C_{25}H_{49}O_2)_2Ba$, is deposited in dense, reticulated crystals. The *magnesium salt* is not deposited when magnesium acetate is added to boiling alcoholic cerotic acid solution (1 per cent.), but, if the liquid is cooled to 50° , a copious precipitate is formed, which does not redissolve on boiling; a mixture of cerotic and melissic acids gives an immediate precipitate with magnesium acetate under these conditions. The *silver salt* is flocculent. Melissic acid resembles cerotic acid in appearance, but crystallises more readily, is almost insoluble in warm methylic alcohol and ether, and melts at 90.6° (corr.). The *methylic* and *ethylic salts* resemble the corresponding cerotates and melt at 74.5° and 73° respectively; the ethylic salt is more readily soluble in ether than the free acid.

J. B. T.

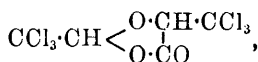
Glyceric Cerotates and Melissates. By THEOD. MARIE (*J. Pharm.*, 1896, [6], 3, 171—177; compare preceding abstract).—Glyceric cerotates and melissates are readily prepared by heating glycerol with cerotic and melissic acids, but apparently they do not occur naturally. *Glyceric cerotate*, $C_{24}H_{46} \cdot COO \cdot C_3H_5(OH)_2$, formed by heating the compounds during 10 hours at $178-180^{\circ}$, is readily soluble in alcohol, ether, and benzene, crystallises in laminæ composed of slender needles, and melts at 78.75° . It is also obtained by the action of silver cerotate on chlorhydrin at 180° . The *dicerotate*, prepared by heating glycerol and the acid at 220° during six hours, resembles the preceding compound, but is less soluble, and melts 79.5° . The *tricerotate* crystallises in slender needles, melting at $76.5-77^{\circ}$. Cerotic acid and the monocerotate are formed by heating trichlorhydrin and silver cerotate at $150-160^{\circ}$; below this temperature, the compounds do not interact. *Glyceric melissate*, $C_{25}H_{49} \cdot COO \cdot C_3H_5(OH)_2$, is prepared in the same manner as the cerotate, which it closely resembles, and melts at $91.5-92^{\circ}$. The *dimelissate* and *trimelissate* resemble the corresponding cerotates, and melt at 93° and 89° respectively.

J. B. T.

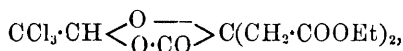
Alloisomerism, a Rejoinder to Michael. By CARL T. LIEBERMANN (*J. pr. Chem.*, 1896, [2], 53, 255—256).—Michael's laws of alloisomerism (this vol., i, 133) cannot be brought into accord with some of the author's experimental results; it is the laws that are at fault.

A. G. B.

Action of Chloral on Hydroxy-acids in Presence of Sulphuric acid. By LAZAR EDELEANU and AL. ZAHARIA (*Chem. Centr.*, 1895, ii, 212—213; from *Bul. Soc. Sci. fizice Bucur România*, 4, 13—15).—Wallach has shown that in presence of sulphuric acid the interaction of chloral and α -hydroxy-acids is represented by the equation, $\text{OH}\cdot\text{CHR}\cdot\text{COOH} + \text{CCl}_3\cdot\text{CHO} = \text{CCl}_3\cdot\text{CH} < \begin{smallmatrix} \text{O}\cdot\text{CHR} \\ \text{O}\cdot\text{CO} \end{smallmatrix}$. Ethylic α -hydroxy- β -trichloropropionate and chloral yield the compound,

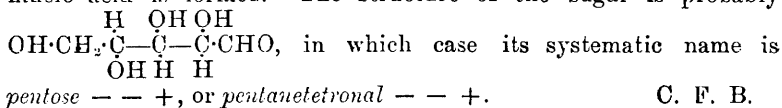


which melts at 114—115°. Ethylic hydrogen sulphate is also formed. Ethylic citrate under similar conditions gives the compound,



which melts at 73°. The *methylic* derivative is oily, and readily reacts with phenylhydrazine. J. B. T.

A New Pentonic acid and Pentose. By EMIL FISCHER and OTTO BROMBERG (*Ber.*, 1896, 29, 581—585).—Xylonic acid prepared by oxidising xylose with bromine, and isolated by means of the double salt which its cadmium salt forms with cadmium bromide, was heated with pyridine for $3\frac{1}{2}$ hours at 135°. Unchanged xylonic acid was then removed as the cadmium double salt, and from the residue the *lactone*, $\text{C}_5\text{H}_8\text{O}_5$, of a new pentonic acid, *lyxonic acid*, was obtained by extraction with ethylic acetate. The lactone melts at 113—114° (corr. 114—115°), and has a specific rotation $[\alpha]_D = +82.4^\circ$ at 20°; it is partly converted back again into xylonic acid when it is heated with pyridine. The *brucine salt* of the acid melts at 174—176° (corr.); the *phenylhydrazide* at 164—165° (corr.). The lactone can be reduced with $2\frac{1}{2}$ per cent. sodium amalgam at 0° to the sugar, *lyxose*, which was obtained as an impure laevorotatory syrup. When its cyanhydrin is prepared and hydrolysed with baryta, and the product oxidised with nitric acid, mucic acid is formed. The structure of the sugar is probably



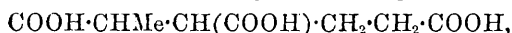
Action of Inorganic acids of the Metals on Organic acids. By ARTHUR ROSENHEIM (*Zeit. anorg. Chem.*, 1896, 11, 225—248).—In order to obtain further information with reference to the constitution of the complex acids derivable from oxalic acid and the acidic oxides of molybdenum, tungsten, vanadium, aluminium, chromium, and iron, the author has determined the conductivities and ionic migration constants of some of these compounds and their salts. The results generally confirm the views put forward in his previous paper (this vol., i, 278). It appears that in these com-

pounds the original avidity of the oxalic acid is much reduced, and that their formation depends on the relative affinities of their components, the one evidently acting as a base towards the other, both together then, in virtue of their acid properties, possessing a residual affinity for strong bases. H. C.

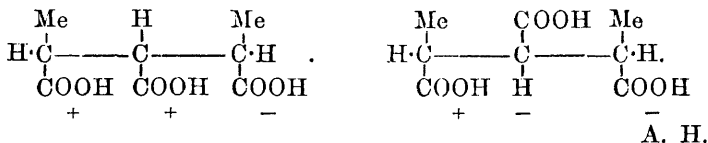
Stereoisomeric Dimethyltricarballic acids. By NICOLAI D. ZELINSKY (*Ber.*, 1896, **29**, 616—618; compare this vol., i, 281).—The electric conductivities of the three inactive dimethyltricarballic acids previously described by the author fit into the series of substituted tricarballic acids, the numbers being as follows.

Tricarballic acid	—	0.022
Methyltricarballic acid...	—	0.032
	M. p.	
Dimethyltricarballic acid.	{ 148—149°	0.051
	{ 175—176	0.054
	{ 203—204	0.042

If one of the acids were a methylcarboxyadipic acid,



it is probable that the conductivity would be less than is required for this series; the author therefore believes that the three substances are stereoisomeric, and supposes that in addition to the racemic form of the fumaroid acid, two inactive malenoid forms may exist.



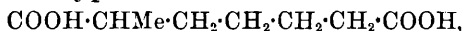
A Contribution to Nomenclature. By M. M. RICHTER (*Ber.*, 1896, **29**, 586—608).—The author publishes proposals for a uniform system of chemical nomenclature for ring compounds and their derivatives, largely supplementary to the proposals of the Geneva Congress (1892). He does this in deference to the wishes of Beilstein and others, who desire that his system should be publicly discussed, in order that by this means the way may be prepared for the introduction at a future congress of a consistent and satisfactory system of nomenclature. It is impossible to give a satisfactory abstract of the paper; those interested must consult the original. It may be said, however, that trivial names are entirely discarded in the case of compounds of known structure, and strictly systematic names are introduced instead; benzene, for example, is “(6)hexene,” and pyrroline is “(5)penteneazene (1).” Ring compounds are chiefly dealt with, the Geneva Congress having already considered open chain compounds in some detail. Rings of 3, 4, 5, 6, 7, members are denoted propene, butene, pentene, hexene, heptene, These names are themselves used if all the members of the ring are CH groups; other elements or groups present are indicated by the addition of the fol-

lowing affixes, which are to be used in the order given if groups of more than one kind are present. O, oxene; S, sulphene; Se, selenene; NH, azene; PH, phosphene; SO₂, sulphonene; N, azine; P, phosphine; As, arsine; I^{'''}, iodine; I^v, iodonium; N^v, azonium. The numbering of the rings is very carefully carried out, each member, without exception, receiving a number. The position of groups in the ring itself is indicated by a number placed in brackets, whereas a number without brackets is used to indicate the position of a substituting group of the ordinary kind; in each case the number *follows* the name of the group to which it applies. α -Methylpyridine, for example, would be "(6) hexeneazine (1)-methyl-2." In the case of mixed open and closed chain compounds, an elaborate scheme is developed, by means of which it is possible to indicate without ambiguity the position of any substituting group; when it is necessary to distinguish positions in a ring from those in an open chain, the numbers referring to the ring have a ^o placed over them; thus, C₆H₅·CH₂·CH₂Cl would be "(6) hexene-ethyl-1^o-chlor-1²," meaning that the chlorine atom is attached to the second carbon atom of an ethyl chain that is joined to the carbon atom 1 of the ring. If two or more chains branch from one carbon atom, positions in the largest are denoted by a simple index, for example, ²; those in the next and in the smallest respectively by a singly and doubly underlined index, for example 2 and 2. This system makes it possible to name at once any compound the existence of which can be foreseen as possible.

The great advantage of the system would be that ring compounds could be named readily, and without ambiguity. The names are, however, sometimes too cumbrous even for the purpose of indexing; it is proposed that for this purpose compounds should be first classified according to their aggregate molecular formulæ, as is done in the author's *Tabellen der Kohlenstoffverbindungen*; under every such formula would be arranged the various compounds to which it corresponds.

C. F. B.

The Hexamethylene Series. IV. Synthesis of Heptanaphthene. By NICOLAI D. ZELINSKY and A. GENEROSOFF (*Ber.*, 1896, **29**, 729—733).— α -Methylpimelic acid,



is prepared from ethylic α -cyanopropionate by the action of trimethylenic bromide and alcoholic sodium ethoxide and then treating the product, which boils at 160—163° (13 mm. pressure), with ethylic sodiomalonate. The *ethylic* salt, C₁₆H₂₅NO₆, thus obtained boils above 170° (75 mm. pressure), and yields the methylpimelic acid when boiled with sulphuric acid. The acid boils at 223—224° (15 mm. pressure), and melts at 57—58°. It has a conductivity (*K*) of 0.00315, and is tribasic to baryta water. *Methylketo*hexamethylene, CHMe·CH₂·CH₂·CO—CH₂·CH₂, is obtained by distilling the acid with quicklime. It is a colourless liquid with a pleasant odour, boils at 165—166°, and has the sp. gr. = 0.9246 at 18°/4°. It readily yields an additive compound with sodium hydrogen sulphite. When reduced, it is con-

verted into the *alcohol*, which boils at 168—169°, and has a sp. gr. 0.9225 at 17°/4°. Methylhexamethylene (heptanaphthene), C_7H_{14} , is formed when the alcohol is reduced with hydriodic acid at 230°. It boils at 101—102°, has the molecular refraction 32.36, and behaves in every way as a saturated hydrocarbon. It appears to be identical with the heptanaphthene isolated by Milkowsky (*Journ. Rus. Chem.*, **17**, [2], 38; **15**, 554), and the hexahydrotoluene of Markownikoff (*J. pr. Chem.*, 1894, 431). When treated with aluminium bromide and bromine, it yields pentabromotoluene.

A. H.

Acids obtained in refining Petroleum. By FUCHS and SCHIFF (*Chem. Zeit.*, 1895, **19**, 1469).—In the hope of turning to account the fruit-like odours of ethereal naphthenecarboxylates, the authors have investigated the alkaline residues obtained from an Austrian refinery. The oils obtained were readily saponified by soda-lye, yielding a soap with a disagreeable odour of fatty acids. The acids, obtained on decomposing the soap, consisted of an octonaphthene-carboxylic and a nononaphthene-carboxylic acid, the latter preponderating. The mixed acids were converted into their ethylic salts, and separated into two fractions boiling at 215—225° and 225—235° respectively. The ethylic salts had, in the concentrated state, a pleasant fruity odour, which, however, in a diluted condition, was completely altered in character, becoming unpleasantly reminiscent of snuff. The authors suggest the use of this property as a ready means of discrimination between fatty and naphthenecarboxylic acids.

A. L.

Hydrogenation of Normal Propylbenzene. Pentabromopropylbenzene. By A. E. TCHITCHIBABIN (*J. Russ. Chem. Soc.*, 1894, **26**, 40—45).—The propylbenzene employed for the experiments was prepared by Fittig's method, and its hydrogenation effected by heating it for 24 hours at 270—280° with hydriodic acid of sp. gr. over 2. The most suitable proportion is about 0.6 c.c. of the substance and 20 c.c. of the acid; the product, which distilled completely at about 148°, was purified by treatment in the cold with fuming nitric acid, and after washing and drying, subjected to repeated fractional distillation. The main fraction, boiling at 140—142°, formed about half of the whole product, and on analysis and a determination of the vapour density, was found to have the formula C_9H_{18} . Its sp. gr. = 0.7819 at 0°/0°.

The action of bromine on propylbenzene in the presence of aluminium bromide, gives rise to pentabromopropylbenzene. The presumption that, under the same conditions the hydrocarbon, C_9H_{18} , would give a pentabromo-derivative was not verified, a crystalline substance being obtained, melting at 230°, and soluble in ether or benzene, less so in hot, and almost insoluble in cold alcohol. A bromine determination indicated the formula $C_9H_9Br_3$, and from its melting point, appearance, and solubility it would appear to be identical with tribromopseudocumene. If this be so, the presence of hexahydro-pseudocumene in the hydrocarbon, C_9H_{18} , can only be explained by the action of iodine, set free during the process of hydrogenation.

An analogous case has been noticed by Rayman and Preiss (*Abstr.*, 1884, 1311), who obtained a series of aromatic hydrocarbons by the action of iodine on cymene. On the other hand, although the specific gravity of hexahydropseudocumene, namely, 0.7812, is very near that of the product obtained by hydrogenation, the difference in the boiling points (hexhydropseudocumene 135—138°, the other compound 142°) is too considerable for them to be identical. S. G. R.

The Benzene Nucleus. By WILHELM VAUBEL (*J. pr. Chem.*, 1896, [2], 53, 241—245; compare *Abstr.*, 1894, i, 325, 501; 1895, i, 53, 339; this vol., i, 213).—The author explains, by the light of his configuration for benzene, certain cases in which meta-derivatives are formed when ortho- and para- may be reasonably expected, certain extraordinary changes on the part of meta-derivatives, and the changes incident to the complete chlorination of benzene and its homologues. A. G. B.

Nitration of Bromobenzene. By JOHN H. COSTE and ERNEST J. PARRY (*Ber.*, 1896, 29, 788—792).—The authors have investigated the preparation of bromonitrobenzenes under varying conditions. The para-compound readily dissolves when boiled with dilute methylated spirit (1 : 1); but at the ordinary temperature its solubility is only 0.1 gram in 100 c.c.; the ortho-compound is much more readily soluble, and is gradually deposited from the mother liquor; after treatment in this manner, the fractions show the correct melting point. (1) Fuming (red) nitric acid (20 c.c.) is heated on the water bath, and bromobenzene (10 c.c.) gradually added below the surface of the acid. The total yield is 66.3 per cent. of the theoretical; para : ortho = 1 : 0.53. (2) Conditions as before, but the experiment conducted at the ordinary temperature. The total yield is 95.2 per cent. of the theoretical; para : ortho = 1 : 0.65. The poor yield in the first experiment was due to the readiness with which both compounds volatilise either when heated alone at 100°, with steam, or with acid vapours. (3) Nitric acid (sp. gr. = 1.42, 15 c.c.) is mixed with concentrated sulphuric (15 c.c.) and bromobenzene (10 c.c.) added to the well-cooled liquid; when the action slackens, it is completed by gently warming. The total yield is 97.7 per cent. of the theoretical; para : ortho = 1 : 0.44. (4) Bromobenzene (20 c.c.) is mixed with glacial acetic acid (20 c.c.) and nitric acid (20 c.c.), and heated until the liquid becomes clear, concentrated sulphuric acid (20 c.c.) is then added, nitrous anhydride is copiously evolved, and the action is completed in about five minutes. The yield is 89.4 per cent. of the theoretical; para : ortho = 1 : 0.51. Attempts to prepare the nitro-bromobenzenes from the nitracetanilides were unsatisfactory; the yield was poor, and the products difficult to purify. Bromobenzene, when heated for some time with ordinary concentrated nitric acid, yields only traces of nitro-derivatives. J. B. T.

Derivatives of Unsymmetrical Tribromobenzene. By C. LORING JACKSON and F. B. GALLIVAN (*Amer. Chem. J.*, 1896, 18, 238—252).—The main facts have already appeared (*Abstr.*, 1895,

i, 212). *Tribromaniline sulphate*, $C_6H_2Br_3 \cdot NH_3SO_4H$ [$Br_3 : NH_3SO_4H = 2 : 4 : 5 : 1$], crystallises from water in white plates, and from alcohol in needles. The corresponding *chloride* and *bromide* crystallise from alcohol in white, branching needles. $2 : 4 : 5$ -*Tribromacetanilide* melts at 188° , and crystallises from alcohol in microscopic, radiating needles. J. F. T.

Isomeric Phenylnitromethanes. By ARTHUR R. HANTZSCH and OTTO W. SCHULTZE (*Ber.*, 1896, **29**, 699—703).—Phenylnitromethane (exonitrotoluene) is best prepared by adding silver nitrite to an ethereal solution of benzylic iodide at 0° ; the yield is 30 per cent. of the theoretical. From its sodium salt, it is set free by acetic acid or carbonic anhydride in the form of an oil, as is well known; mineral acids liberate, at not too high a temperature, white crystals which melt at 74 — 76° . These represent an isomeric form of the oily substance; they are transformed into the latter when heated to the boiling point in ethereal or alcoholic solution, or if allowed to remain at the ordinary temperature in contact with hydrochloric acid, or in solution in benzene. The crystalline differs from the oily isomeride in that it gives a reddish-brown coloration with ferric chloride, and it also dissolves much more readily in aqueous alkali carbonates, no carbonic anhydride being evolved, however. It is suggested that the new isomeride has the constitution $CHPh < \begin{smallmatrix} N \cdot OH \\ | \\ O \end{smallmatrix}$, and that, when an ordinary nitro-paraffin forms a sodium salt, it undergoes a molecular transformation into an isomeride with a structure similar to this. The new substance is certainly not identical with benzhydroxamic acid, $OH \cdot CPh : NOH$. C. F. B.

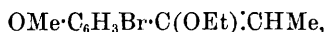
Combination of Aluminium Chloride with Phenols and their Derivatives. By G. PERRIER (*Compt. rend.*, 1896, **122**, 195—198).—Ketones, nitriles, ethers, &c., combine with aluminium chloride in the proportion of 2 mols. of the former to 1 mol. of the latter, without any elimination of hydrogen chloride, the products being additive compounds. Phenols behave differently, for whilst the molecular proportions remain the same, 2 mols. of hydrogen chloride are eliminated, and substitution products of the composition $Al_2Cl_4(OR')_2$ are formed. In presence of water, the original phenol is regenerated, and basic aluminium chloride, $Al_2Cl_4(OH)_2$, is formed. All the compounds are solid, and some of them crystallise readily; they are insoluble in carbon tetrachloride and light petroleum, but the solubility in carbon bisulphide or alcohol varies with the nature of the phenol. The aluminium chloride and the phenol are mixed directly or in presence of carbon bisulphide, and the mixture is heated towards the close of the reaction.

The products have the following characteristics: *Phenol*, white crystals, which melt at 181 — 183° , and decompose at about 200° , very soluble in carbon bisulphide and alcohol; *ortho*-nitrophenol, red needles, which melt at 160 — 165° , slightly soluble in alcohol and carbon bisulphide; *para*-nitrophenol, a yellow powder which melts at 99 — 100° , and decomposes at about 105° , insoluble in carbon bisulphide, but soluble

in alcohol; *orthochlorophenol*, a white, crystalline powder, which melts at 207—210°, and is soluble in alcohol, but only slightly soluble in carbon bisulphide; *parachlorophenol*, colourless crystals, melting at 185—187°, soluble in alcohol and somewhat soluble in carbon bisulphide; *thymol*, colourless crystals melting at 142—145°, and decomposing at 150°, very soluble in carbon bisulphide and in alcohol; α -*naphthol*, small, red crystals, almost insoluble in carbon bisulphide; β -*naphthol*, a yellow powder, likewise insoluble in the bisulphide; *salicylaldehyde* and *methylic* and *phenylic salicylates* yield yellowish products insoluble in carbon bisulphide. C. H. B.

Water of Crystallisation of Barium Picrate. By HUBERT G. SHAW (*Amer. Chem. J.*, 1896, **18**, 266—268).—A specimen of barium picrate examined by the author contained 6H₂O. The amount has been variously stated as 4H₂O, 5H₂O, and 6H₂O. Experiments will be made to ascertain if more than one hydrate exists. J. F. T.

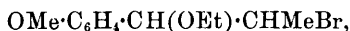
Action of Sodium Ethoxide on Anethoil and Monobrom-anethoil Dibromides. By CARL HELL and A. HOLLENBERG (*Ber.*, 1896, **29**, 682—690; compare Wallach and Pond, this vol., i, 94).—When monobromanethoil dibromide, OMe·C₆H₃Br·CHBr·CHMeBr, is boiled with alcoholic sodium ethoxide, an oily compound,



boiling at 180—182° under 16 mm. pressure, is obtained. When this compound is treated with acids or with water, or even when it is allowed to remain in contact with air, it becomes hydrolysed, losing alcohol and forming the crystalline ketone OMe·C₆H₃Br·CO·CH₂Me; the same substance is formed when it is heated at 270—295° under atmospheric pressure, under which circumstances ethylene is evolved. When treated with bromine (1 mol.), both these compounds yield a ketone, OMe·C₆H₃Br·CO·CHMeBr, melting at 99°, or with 2 mols. of bromine a ketone, OMe·C₆H₃Br·CO·CMeBr₂, melting at 103·5°.

Anethoil itself yields a similar series of compounds. The compound OMe·C₆H₄·C(OEt)·CHMe, is an oil boiling at 135—138° under 13 mm., and at 258—260° under atmospheric pressure.

The action of the sodium ethoxide, no doubt, takes place in two stages, as in the case of ethylisoeugenol (this vol., i, 357). In the case of anethoil, the intermediate product,



has been isolated, and forms an oil which boils at 165—170° under 14 mm. pressure, and loses both alcohol and ethylic bromide when heated at 220°. The corresponding bromanethoil compound is decomposed in the same way when distilled under diminished pressure, and has not yet been obtained pure. C. F. B.

Certain Bromine Derivatives of Resorcinol. By C. LORING JACKSON and F. L. DUNLAP (*Amer. Chem. J.*, 1896, **18**, 117—132).—It has been observed (*Amer. Chem. J.*, **15**, 641) that the diethyl ether of tribromonitroresorcinol, NO₂·C₆Br₃(OEt)₂, when heated with sodium

ethoxide, exchanges 2 atoms of bromine for hydrogen, giving $\text{NO}_2 \cdot \text{C}_6\text{H}_2\text{Br}(\text{OEt})_2$. The diethyl ether of tribromoresorcinol, however, does not give up bromine to sodic ethoxide at the boiling point of alcohol, and the dibrom-ether is not attacked below 200° , and is, therefore, more stable than 1 : 3 : 5-tribromobenzene, which is slowly converted into dibromanisole at $120\text{--}130^\circ$ (Blau, Abstr., 1887, 242). From tribromoresorcinol, bromine could be removed with great ease, even water at 100° decomposing it. Ethoxyl groups, therefore, do not weaken the attachment of the bromine atoms to the benzene ring, whereas hydroxy-groups exert this loosening action to the same extent as the nitro-groups in tribromodinitrobenzene.

The brown amorphous substances produced by removing bromine from tribromoresorcinol could not be analysed, but appear to be substituted resorcinol ethers, formed by a reaction involving the hydroxyl groups. Ethylic sodiomalonate gave a similar unmanageable product with tribromoresorcinol, but, in addition to this, ethylic ethanetetra-carboxylate was isolated.

Tribromoresorcinol diethyl ether is converted by nitric acid into the 2 : 4 : 6 : 5-tribromonitroresorcinol diethyl ether, melting at 101° . The action of nitric acid on dibromoresorcinol diethyl ether was quite different, giving a new *dinitroresorcinol diethyl ether*, melting at 126° , two nitro-groups displacing two bromine atoms. A similar replacement occurred when the tribromoresorcinol was treated with fuming nitric acid, the product being the bromodinitroresorcinol described by Typke (Abstr., 1883, 915) and Fèvre (*ibid.*, 733).

It is thus proved that hydroxyl and ethoxyl have the same effect on bromine that they have on hydrogen attached to the benzene ring; for just as phenols are much more susceptible to the replacement of their hydrogen by halogens, or nitro-groups than the corresponding hydrocarbons, so the bromine can be replaced by other radicles, including the nitro-group, much more easily in tribromoresorcinol than in tribromobenzene; whilst, on the other hand, the phenol ethers hold their hydrogen or bromine as firmly as the corresponding hydrocarbons. The only exception is the replacement of bromine by NO_2 , when nitric acid acts on dibromoresorcinol diethyl ether. Towards other reagents, however, such as sodium ethoxide, the dibromo-ether shows the same stability as the tribromo-ether.

The debromination of tribromoresorcinol diacetate was attempted, but it was converted into tribromoresorcinol by the reagents used, and consequently the products were the same as those above mentioned. With fuming nitric acid, the diacetate gives *tribromonitroresorcinol diacetate*, which crystallises in yellowish-white prisms, and melts at 161° . The *sodium derivative* of tribromoresorcinol was obtained in short, flat, white prisms by precipitating an ethereal solution with alcoholic sodium ethoxide, and apparently contained 2 mols. of alcohol of crystallisation. After standing for a short time, even in a vacuum or in hydrogen, it suddenly turned black, evolving alcohol vapour and developing heat; the black residue gave up to water sodium bromide and a black salt, but neither this nor the red, amorphous substance left undissolved could be analysed.

Dibromoresorcinol diethyl ether, $\text{C}_6\text{H}_2\text{Br}_2(\text{OEt})_2$, prepared by adding

bromine to a solution of resorcinol diethyl ether in glacial acetic acid, crystallises in long, slender, white, silky prisms, and melts at 99—100°. *Tribromoresorcinol diethyl ether*, prepared from the foregoing with excess of bromine, crystallises in long, pearly fibres, and melts at 68—69°. *Tribromoresorcinol*, prepared by Benedikt's method (*Monatsh.*, **4**, 227), was found, after recrystallisation from water, to have the melting point given by him, whereas Typke (*Ber.*, **10**, 1578) gives 104°. Hlasiwetz and Barth state that it crystallises with 2H₂O, but it was found to be anhydrous. *Tribromoresorcinol* is gradually decomposed by boiling water, bromine being removed, and a dark red, amorphous substance formed. Aniline and sodium ethoxide also remove bromine, but in none of these cases could any organic product be isolated in a state fit for analysis. A. E.

Derivatives of Veratrol. By FR. BRÜGGMANN (*J. pr. Chem.*, 1896, [2], **53**, 250—254).—*Tetrachloroveratrol*, C₆Cl₄(OMe)₂, prepared by chlorinating veratrol in carbon tetrachloride, crystallises from alcohol in white needles, and melts at 88°; when heated with excess of strong sulphuric acid, it is converted into *tetrachloroguaiacol*, (OH)C₆Cl₄(OMe), which melts at 185—186°.

Tetrabromoveratrol is prepared by the action of excess of bromine on a solution of veratrol in strong sulphuric acid; it crystallises from ether in white needles, and melts at 118°. Strong sulphuric acid does not convert it into a guaiacol.

Diiodoveratrol, C₆H₂I₂(OMe)₂, prepared by the action of iodine and mercuric oxide on an alcoholic solution of veratrol, crystallises in white needles, and melts at 125°.

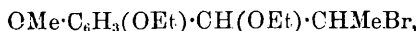
By nitrating a sulphuric acid solution of veratrol, a *dinitroveratrol*, C₆H₂(NO₂)₂(OMe)₂, is obtained, which crystallises in yellowish-brown needles, and melts at 127—128°. By heating nitroveratrol with strong nitric acid in a sealed tube, a second dinitroveratrol, crystallising in yellow needles and melting at 127°, is obtained; this is probably identical with Merck's dinitroveratrol. The isomerism of the two dinitroveratrols is confirmed by the fact that 100 c.c. of alcohol at 15° dissolve 0.3892 gram of the compound melting at 127—128°, and 0.2660 of that melting at 127°.

Benzoylveratrol, C₆H₃Bz(OMe)₂, is formed by the action of benzoic chloride on veratrol in presence of aluminium chloride; it crystallises in aggregates of white needles, and melts at 99°; the *phenylhydrazone* of this compound melts at 174°. An acetyl analogue could not be prepared. *Benzoylguaiacol*, OMe·C₆H₄·OBz, melts at 57°.

Veratrol thioanilide, C₆H₃(OMe)₂·CS·NHPh, obtained by the action of phenylthiocarbimide on veratrol, in presence of aluminium chloride, crystallises in slender, felted, yellow needles, and melts at 159°. Oxidation with potassium ferricyanide converts it into the compound C₆H₃(OMe)₂·C<N>S<C₆H₄, which crystallises in needles melting at 132°. The thioanilide is desulphurised by iodine in alcohol, yielding the *veratranilide*; this crystallises in white, felted needles, and melts at 154°. A. G. B.

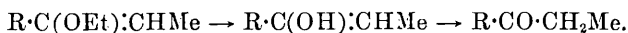
Pyrogallol. By R. GODEFFROY (*Chem. Centr.*, 1895, ii, 159; from *Zeit. Österr. Apoth. Verein*, **33**, 377—380; *Pharm. Zeit.*, **40**, 390).—The compound $\text{OH}\cdot\text{C}_6\text{H}_3\text{O}_2\text{Ba} + 4\text{H}_2\text{O}$ is deposited in colourless needles, when aqueous pyrogallol is mixed with baryta water in excess; it rapidly blackens when exposed to air, and decomposes when boiled with water. Alcoholic pyrogallol yields a similar compound with $3\text{H}_2\text{O}$. J. B. T.

Action of Sodium Ethoxide on Ethylisoeugenol Dibromide. By CARL HELL and B. PORTMANN (*Ber.*, 1896, **29**, 676—682; compare *Abstr.*, 1895, i, 657, and Wallach and Pond, this vol., i, 95).—If sodium ethoxide (1 mol.) in alcoholic solution is allowed to act on ethylisoeugenol dibromide (1 mol.), a compound



is obtained as an oil. If this is heated at $225\text{--}230^\circ$, or if it is distilled under 15 mm. pressure, when it appears to boil at $185\text{--}187^\circ$, it loses alcohol, and the compound $\text{OMe}\cdot\text{C}_6\text{H}_3(\text{OEt})\cdot\text{CH}:\text{CHMeBr}$, melting at 72° , is formed. This compound takes up 2 atoms of bromine, the product melting at 107° ; it does not readily exchange its bromine atom for other groups, but it reacts with sodium ethoxide, and the product is a compound, $\text{OMe}\cdot\text{C}_6\text{H}_3(\text{OEt})\cdot\text{C}:\text{CHMe}$, which, curiously, only takes up 2 atoms of bromine.

In the light of these facts it is necessary to regard the action of excess of sodium ethoxide on an aromatic propenyl dibromide, with subsequent hydrolysis of the product, as taking place in the following stages: $\text{R}\cdot\text{CHBr}\cdot\text{CHMeBr} \rightarrow \text{R}\cdot\text{CH}(\text{OEt})\cdot\text{CHMeBr} \rightarrow$



Sodium reduces the compound $\text{OMe}\cdot\text{C}_6\text{H}_3(\text{OEt})\cdot\text{CH}:\text{CHMeBr}$ to dihydroethyleugenol, $\text{OMe}\cdot\text{C}_6\text{H}_3(\text{OEt})\cdot\text{CH}_2\cdot\text{CH}_2\text{Me}$, and when potassium acetate acts on ethylisoeugenol dibromide, only one bromine atom is displaced, and a compound, $\text{OMe}\cdot\text{C}_6\text{H}_3(\text{OEt})\cdot\text{CH}(\text{OAc})\cdot\text{CHMeBr}$, is formed, which loses acetic acid when distilled, and forms the compound $\text{OMe}\cdot\text{C}_6\text{H}_3(\text{OEt})\cdot\text{CH}:\text{CHMeBr}$. C. F. B.

Structure of the Product of Oxidation of Paratoluidine. By JACOB N. BARSILOWSKY (*J. Russ. Chem. Soc.*, 1894, **26**, 52—55).—Reference is made to a paper by Green (*Trans.*, 1893, 1395) on the structure of a compound which was originally obtained by the author in 1873, although he has not published his results until now. It was formed, together with paratoluene, by the oxidation of paratoluidine, and had the same elementary composition as azotoluene, namely, $\text{C}_7\text{H}_7\text{N}$. The author obtained the same compound by the oxidation of paratolylparatolylenediamine, $\text{NH}_2\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{NH}\cdot\text{C}_6\text{H}_7$ [1 : 4 : 3]. The mean of several determinations of the molecular weight by Raoult's method, using benzene as solvent, is 310, which agrees with the formula, $(\text{C}_7\text{H}_7\text{N})_3 = 315$, and is also in accordance with the figure found by Green, namely 320.

On heating the hydrochloride of the compound, the hydrochloride of another base is formed, which could not be obtained in a state of

purity, as it rapidly oxidises, forming a dark brown oxy-base, to which the author, as well as Klinger and Pitschke (Abstr., 1885, 151), have assigned the name of *rosotoluidine*. Its molecular weight was found to be 220, corresponding with the formula $C_{14}H_{14}N_2O = 226$.

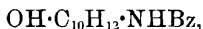
S. G. R.

Condensation of Aldehydes with Aromatic Amines. By JACOB N. BARSILOWSKY (*J. Russ. Chem. Soc.*, 1894, **26**, 51—52).—The results of the author's investigation on the condensation of benzaldehyde, and of the three isomeric nitrobenzaldehydes, with azobenzene (*J. Russ. Chem. Soc.*, 1893, **23**, 47), have led him to conclude that the usual explanation of the action which takes place during the condensation of the above-named aldehydes with the salts of aromatic amines in the presence of zinc chloride is not justified. From a long series of experiments on the condensation, under varied conditions, of these aldehydes with free aniline and its salts in the presence of zinc chloride, it appears that in the first phase of the reaction benzyldene-aniline, $CHPh:NPh$, boiling at 51.5° , and also three isomeric nitrobenzyldeneanilines, ortho-, meta-, and para-, boiling respectively at 89.5° , $64-65^\circ$, and $65-66^\circ$ are formed, which then react with the salts of aniline, giving derivatives of triphenylmethane, namely, diamidotriphenylmethane and three isomeric nitrodiamidotriphenylmethanes.

S. G. R.

Action of Phenylhydrazine on Nitrosophenols. By GIUSEPPE PLANCHER (*Gazzetta*, 1895, **25**, ii, 379—394).—On treating nitrosophenol suspended in benzene with phenylhydrazine, a good yield of paramidophenol is obtained; no azoxyphenol could be extracted from the resinous residue, as was done by Fischer and Wacker (Abstr., 1888, 1286), operating in ethereal solutions.

Paramidothymol is obtained by the action of phenylhydrazine on nitrosothymol in benzene solution; it melts at $177.5-179^\circ$, not at $176-177^\circ$, as stated by Liebermann and Ilinski (*Ber.*, **18**, 3199). Its *hydrochloride*, $OH \cdot C_{10}H_{12} \cdot NH_2 \cdot HCl$, is a white, crystalline substance, melting at 255° ; it gradually evolves hydrogen chloride and turns blue. *Acetamidothymol*, $OH \cdot C_{10}H_{12} \cdot NHAc$, prepared by the aid of acetic anhydride, forms small, white needles, which redden on exposure, and melt at $174-175^\circ$. *Diacetamidothymol*, $OH \cdot C_{10}H_{12} \cdot NAc_2$, obtained by the further action of acetic anhydride, crystallises in colourless scales melting at $88-90^\circ$. *Benzamidothymol*,



crystallises in colourless needles melting at $178-179^\circ$; *benzamido-benzoylthymol*, $OBz \cdot C_{10}H_{12} \cdot NHBz$, crystallises in white needles melting at $166-167^\circ$. *Benzyldeneamidothymol*, $OH \cdot C_{10}H_{12} \cdot N:CHPh$, obtained by heating paramidothymol with benzaldehyde at $120-125^\circ$, crystallises in yellowish prisms melting at $148-150^\circ$; it yields *benzyldene-amidoacetylthymol* (?) when treated with acetic anhydride. Paramidothymol and metabenzaldehyde yield a yellow substance melting at $161-162^\circ$. *Cumyldeneparamidothymol*, $OH \cdot C_{10}H_{12} \cdot N:CH \cdot C_6H_4Pr$, melts at $153-154^\circ$.

A good yield of paramidocarvacrol is obtained by the action of

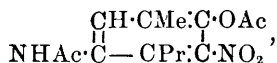
phenylhydrazine on nitrosocarvacrol in benzene solution; its *hydrochloride* melts at 280° with slight previous decomposition, and its *acetyl* derivative, $\text{OH}\cdot\text{C}_{10}\text{H}_{12}\cdot\text{NHAc}$, forms large, colourless crystals, melting at $176\text{--}177^{\circ}$.

1-Nitroso- β -naphthol and hydrazine react in benzene or alcoholic solution, yielding the amido- β -naphthol of Stenhouse and Groves (*Annalen*, **189**, 153). 4-Nitroso- α -naphthol similarly yields Liebermann and Dittler's amidonaphthol, whilst the 2-nitroso- α -naphthol, melting at 152° , gives 2-amido- α -naphthol. W. J. P.

Dinitramidothymol and Dinitramidocarvacrol. By MARIANO SODERI (*Gazzetta*, 1895, **25**, ii, 401—407).—On reducing dinitrothymyl benzoate (Mazzara, *Abstr.*, 1891, 46) with tin and hydrochloric acid, amidobenzamidothymol and *nitramidothymylic benzoate*, $\text{NO}_2\cdot\text{C}_6\text{HMePr}(\text{NH}_2)\cdot\text{OBz}$, are obtained; the latter crystallises in yellow needles melting at $158\text{--}160^{\circ}$, and, on treatment with alcoholic potash, yields *nitramidothymol*, $\text{NO}_2\cdot\text{C}_6\text{HMePr}(\text{NH}_2)\cdot\text{OH}$, which crystallises in long, reddish needles. With acetic anhydride, it gives *acetamidonitrothymylic acetate*, $\text{NO}_2\cdot\text{C}_6\text{HMePr}(\text{NHAc})\cdot\text{OAc}$, which crystallises in small, yellow prisms melting at $157\text{--}159^{\circ}$.

Acetamidobenzamidothymol, $\begin{array}{c} \text{C}(\text{NHAc})\cdot\text{CMe}\cdot\text{C}\cdot\text{N} \\ | \qquad \qquad | \\ \text{CH} \text{---} \text{CPr}\cdot\text{C}\cdot\text{O} \end{array} > \text{CPh}$, obtained by treating amidobenzamidothymol with acetic anhydride, crystallises in white needles melting at $207\text{--}208^{\circ}$. On treating dinitrothymol with acetic anhydride, Mazzara's dinitrothymylic acetate (*loc. cit.*) is obtained.

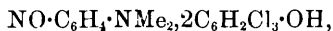
Alcoholic potash acts on nitramidocarvacrylic benzoate, with formation of *nitramidocarvacrol*, $\begin{array}{c} \text{CH}\cdot\text{CMe}\cdot\text{C}\cdot\text{OH} \\ | \qquad \qquad | \\ \text{NH}_2\cdot\text{C} \text{---} \text{CPr}\cdot\text{C}\cdot\text{NO}_2 \end{array}$; this forms beautiful yellow crystals, melting at $134\text{--}135^{\circ}$, and, on treatment with acetic anhydride, yields *acetamidonitrocarvacrylic acetate*,



which crystallises in white needles, melting at $222\text{--}225^{\circ}$.

W. J. P.

Action of Nitrosodimethylaniline on Trihaloid Substituted Phenols. By LAZAR EDELEANU and ENESCU (*Chem. Centr.*, 1895, ii, 218; from *Bul. Soc. Sci. fizice Bucur România*, **4**, 15—19).—Nitrosodimethylaniline and 1 : 3 : 5-trichlorophenol combine when mixed in light petroleum solution, forming the compound



which is highly unstable, melts at $90\text{--}91^{\circ}$, has a green colour in solution, and is readily resolved into its constituents by the action of hydrochloric acid. At the boiling point of alcohol, the above compounds yield azoxydimethylaniline. The corresponding compound from tribromophenol is deposited in bluish-violet crystals, melting at $89\text{--}90^{\circ}$; when boiled with alcohol, the components also yield azoxy-

dimethylaniline. The compound from triiodophenol has not yet been obtained in a pure state. Trichlororesorcinol and nitrosodimethylaniline yield the compound $\text{NO} \cdot \text{C}_6\text{H}_4 \cdot \text{NMe}_2 \cdot \text{C}_6\text{HCl}_3(\text{OH})_2$, which is deposited from benzene in violet crystals melting at 120° .

Triiodophenol was prepared by the interaction of iodine and alkaline phenol solution. On acidifying the liquid, triiodophenol is precipitated, together with a compound which is insoluble in alkali; it is deposited from carbon bisulphide in the form of a blue powder, and melts at $215\text{--}220^\circ$; its composition has not been determined.

J. B. T.

Derivatives of Phenetidine [Paramidophenetoil]. By LUDWIG WENGHÖFFER (*Chem. Zeit.*, 1895, **19**, 1753).—*Benzylparamidophenetoil*, $\text{OEt} \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{C}_7\text{H}_7$, is prepared by warming a mixture of benzylic chloride and paramidophenetoil (2 mols.), and extracting the product with ether. It crystallises in leaflets, and melts at $45\text{--}46^\circ$, dissolves in alcohol, chloroform, and ether, but is insoluble in water. It dissolves without decomposition in hot sulphuric acid, and is not attacked by hot alkalis. It appears to be a valuable febrifuge.

Parethoxyphenyloxamide, $\text{C}_2\text{O}_2(\text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{OEt})_2$, formed by the condensation of oxalic acid and phenetidine (2 mols.) at $140\text{--}145^\circ$, crystallises in needles, and melts at 263° ; it is sparingly soluble in alcohol, benzene, and chloroform, but dissolves readily in acetic acid. Hot caustic soda decomposes it into phenetidine and sodium oxalate. It does not yield an acetyl derivative, being split up into carbonic oxide and paracetamidophenetoil when heated at 200° with acetic anhydride. It is not poisonous.

Paramidophenetoil mandelate forms shining crystals, which dissolve readily in alcohol and hot water, and melt at 105° . When it is heated at $130\text{--}170^\circ$, water is eliminated, and *amygdalyl-4-amidophenetoil*, $\text{OEt} \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{CO} \cdot \text{CHPh} \cdot \text{OH}$, is formed; this crystallises from 60 per cent. alcohol, in white, shining leaflets, dissolves sparingly in hot water and in ether, and melts at 140.5° . It is stable towards dilute alkalis and acids, but is decomposed by strong sulphuric acid. Both this compound and its *acetyl derivative* have antipyretic and antiseptic properties. The latter substance melts at 154° , dissolves readily in alcohol and in acetic acid, but is only sparingly soluble in ether and hot water; it is readily hydrolysed by alkalis.

Ethylic acetoacetate condenses very readily with paramidophenetoil to form *ethylyc β -phenetidylcrotonate*; this crystallises from hot methylic alcohol in glistening, white leaflets, melting at $52.5\text{--}53^\circ$, and is insoluble in water, but soluble in alcohol and ether; dilute acids decompose it into paramidophenetoil and ethylyc acetoacetate. When heated slowly, varying quantities of diparethoxyphenylcarbamide are produced, but when it is quickly heated to $225\text{--}240^\circ$, alcohol is eliminated, and the product consists almost entirely of *4'-hydroxy-4-ethoxy-2'-methylquinoline*, $\text{OEt} \cdot \text{C}_8\text{NH}_2 \cdot \text{Me} \cdot \text{OH}$; this crystallises from absolute alcohol in silky, white leaflets, dissolves with difficulty in cold water and ether, more readily in hot water, and is very soluble in alcohol. It forms salts with acids, the *hydrochloride*,

$C_{12}H_{13}NO_2 \cdot HCl$, crystallising from alcohol in slender, felted needles, the *platinochloride* forming brittle, yellow crystals. It has a bitter, not unpleasant taste, and has strongly marked antipyretic properties.

A. L.

Constitution of Aromatic Diazo-compounds and their Isomerides. By CHRISTIAN W. BLOMSTRAND (*J. pr. Chem.*, 1896, [2], 53, 169—197).—A discussion of the present controversy on the subject indicated in the title, with reference to the views originally offered by the author (Abstr., 1875, 571).

A. G. B.

Azophenylethyl [Benzeneazoethane] and Acetaldehyde-phenylhydrazone. By EMIL FISCHER (*Ber.*, 1896, 29, 793—797).—The work of Thiele and Heuser (this vol., i, 340) has led them to the conclusion that the complex $N:N \cdot CH$ is not capable of existence, but changes immediately into the hydrazo-form, $NH \cdot N:C$. The author has previously described (*Annalen*, 199, 328) benzeneazoethane, $PhN:NEt$, and has also prepared acetaldehydephenylhydrazone, and, as this is the only example of the simultaneous existence of compounds of both types, the subject has been re-investigated.

Benzeneazoethane is obtained in the manner previously described; it may also be prepared by the action of mercuric oxide on ethylphenylhydrazine; the tetrazone is removed by crystallisation, and the azo-compound, after treatment with dilute hydrochloric acid, fractionated under reduced pressure; it boils at $88-93^\circ$ ($20-25$ mm.), and the molecular weight agrees with the formula. The characteristic odour of the compound is most apparent when it is warmed with water; it is soluble at the ordinary temperature in concentrated hydrochloric acid and in sulphuric acid (1:1); when warmed, the solution suddenly boils; this was previously described as effervescence; when dissolved in sulphuric acid (60 per cent. 10 parts), and the solution allowed to remain during 15 minutes at the ordinary temperature, acetaldehydephenylhydrazone is formed; the same change probably occurs in dilute acid solution as on warming with dilute sulphuric acid, the azo-compound yielding phenylhydrazine and acetaldehyde; probably acetaldehydephenylhydrazone is first produced. With dilute hydrochloric acid, the changes are more complex; phenylhydrazine is formed in comparatively small quantity, together with a considerable amount of resinous matter.

Acetaldehydephenylhydrazone, previously termed ethylidenephylhydrazine (*Annalen*, 190, 136 and 236, 137) exists in two or more forms, and is most conveniently purified by distillation; it boils at $140-150^\circ$ ($20-30$ mm.), and crystallises from alcohol (75 per cent.) at 0° in colourless, lustrous plates melting at $66-69^\circ$; after remaining some hours in a vacuum the melting point falls to $63-65^\circ$; it is stable in a vacuum over sulphuric acid, but on exposure to moist air speedily becomes yellow, then red; it is soluble in 6 parts of light petroleum (b. p. $55-75^\circ$), and then melts at 80° ; whether this is a mixture of the β -form (m. p. $66-65^\circ$) with the α -form (see below), or a distinct modification, is uncertain. The α -modification is prepared by boiling the β -compound for a few moments in dilute alcoholic solution with a little soda; it crystallises in long, colourless prisms, melts at $98-101^\circ$,

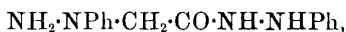
is stable in dry air, and soluble in about 20 parts of light petroleum; the yield is 60 per cent. When recrystallised, it usually retains its melting point, but, under certain conditions which have not been determined, the melting point suddenly falls to 80°. By distillation under 20 mm. pressure, the α -compound is reconverted into the β -derivative; the distillate, when recrystallised from alcohol, melts at about 80°, but, after 24 hours, at 64–65°. Both compounds are extremely stable towards sodium amalgam, being scarcely changed even after 24 hours' action, except that the β - is converted into the α -form. The compounds have identical molecular weights, agreeing with the formula $C_8H_{10}N_2$. J. B. T.

Metallic Normal Diazo-salts. By EUGEN BAMBERGER (*Ber.*, 1896, 29, 564–577).—Hantzsch's statements (*Abstr.*, 1895, i, 516, 664) as to the behaviour of metallic salts of diazobenzenesulphonic acid are devoid of foundation. It is not true that the mixture of the acid with 1 equivalent of a base gives off no nitrogen at 0° while it is becoming neutral, neither is it true that its power of forming azo-dyes suffers no diminution under these circumstances. Nor is it true that the neutral solution eventually loses all its nitrogen, whereas the acid by itself, or when mixed with an excess (2 equivalents) of base, loses none; as a matter of fact, the neutral solution only loses about two-thirds of its nitrogen, even at 100°, but the solution of the acid itself loses practically all its nitrogen at that temperature. Nor is it true that the solution of the salt, $SO_3Na \cdot C_6H_4 \cdot N_2 \cdot ONa$, requires at first only 1 equivalent of acid to neutralise it, but eventually uses up 2 equivalents if the solution is allowed to remain until the acid reaction, caused by excess of acid, has disappeared, and more acid is then added in the same way, until a permanent acid reaction is obtained. As a matter of fact, much more than 1 equivalent of acid is invariably required to produce neutrality; apparently 2 equivalents represent the amount theoretically necessary, but often rather less suffices, presumably because a partial isomerisation of the salt takes place. Hantzsch's data being thus entirely erroneous, the arguments which he bases upon them for the existence of two geometrically isomeric varieties of diazo-salts—*syn* and *anti*—in addition to the diazonium salts, fall to the ground. C. F. B.

Diazoacetophenone. By ANGELO ANGELI and ENRICO RIMINI (*Gazzetta*, 1895, 25, ii, 494–497).—Angeli has shown (*Abstr.*, 1893, i, 570) that diazoacetophenone, $CPhO \cdot CH:N_2$, is formed by the action of nitrous acid on amidoacetophenone hydrochloride; an improved method for preparing this diazo-compound is now given. It separates from hot light petroleum in long, flattened, yellow crystals, having a characteristic odour; it melts without decomposition at 50°, but above this temperature, it decomposes with evolution of gas; when rapidly heated, it explodes violently, leaving a white powder which is almost insoluble in all solvents. Diazoacetophenone has all the properties of an aliphatic diazo-compound; it is fairly stable towards alkalis, but with acids readily gives up its nitrogen, and with sulphuric acid the decomposition proceeds explosively. It is readily

converted into phenacyl bromide by hydrogen bromide, and yields benzoic acid when treated with sodium carbonate. W. J. P.

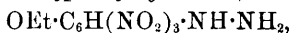
Asymmetric Phenylhydrazine Derivatives. By HANS RUPE and GEORG HEBERLEIN (*Ber.*, 1896, **29**, 622—623; compare *Abstr.*, 1895, i, 521).—The compound of *as*-phenylhydrazidoacetanilide is decomposed by the action of concentrated sulphuric acid with formation of 1-phenyl-3-methyl-5-ketotetrahydropyridazine-4-carboxylic acid, $\text{NPh} \begin{smallmatrix} \text{N} \cdot \text{CMe} \\ \text{CH}_2 \cdot \text{CO} \end{smallmatrix} > \text{CH} \cdot \text{COOH}$, which decomposes at 230°. Phenylhydrazine reacts with chloracetamide to form *as*-phenylhydrazidoacetamide melting at 140°. The benzaldehyde compound melts at 225°. The same compound may be prepared by the reduction of nitrosoanilido-acetamide by means of zinc and acetic acid. When phenylhydrazine acts on chloracetamide, a second compound is also formed; this substance is *as*-phenylhydrazido-acetophenylhydrazide,



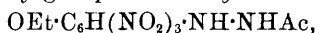
and melts at 178°; it is also formed when phenylhydrazidoacetamide is heated with phenylhydrazine. Its benzaldehyde compound melts at 196°. A. H.

Action of Hydrazine Hydrate on the Ethylic Derivatives of some Nitrophenols. Synthesis of 2:4:6-Trinitromethoxyphenylhydrazine. By ATTILIO PURGOTTI (*Gazzetta*, 1895, **25**, ii, 497—504).—Picrylhydrazine is gradually deposited from an alcoholic solution of hydrazine hydrate and ethylic picrate; ethylic 2:4-dinitrophenol behaves similarly.

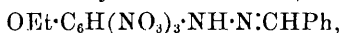
2:4:6-Trinitromethoxyphenylhydrazine,



prepared by mixing trinitroresorcinol ethyl ether and hydrazine hydrate in ethereal alcoholic solution, crystallises in small, yellow needles melting at 173°; it gives the iodoform reaction, and therefore contains an ethoxy-group. Its acetyl derivative,



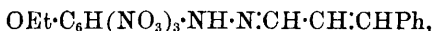
produced on boiling it with acetic acid, crystallises in yellow needles melting at 179°, and its benzylidene derivative,



prepared by boiling with acetic acid and benzaldehyde, is obtained in minute yellow needles melting at 228°.

Orthohydroxybenzylidene-2:4:6-trinitromethoxyphenylhydrazine, $\text{OEt} \cdot \text{C}_6\text{H}(\text{NO}_2)_3 \cdot \text{NH} \cdot \text{N} \cdot \text{CH} \cdot \text{C}_6\text{H}_4 \cdot \text{OH}$, is prepared in a similar manner and forms thin, yellow, crystals melting at 217—218°. The *para*-hydroxy-isomeride separates in small, red crystals melting at 231°.

Cinnamylidene-2:4:6-trinitromethoxyphenylhydrazine,

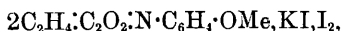


forms a red crystalline powder melting at 200—201°.

W. J. P.

Action of Iodine on Imides and Substituted Imides. By ARNALDO PIUTTI (*Gazzetta*, 1895, 25, ii, 518—527).—A compound of paraethoxyphenylsuccinimide, potassium iodide, and iodine, of the composition, $2 \begin{array}{c} \text{CH}_2\text{CO} \\ | \\ \text{CH}_2\text{CO} \end{array} > \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{OEt}, \text{KI}, \text{I}_2$, is obtained by warming the constituents in dilute acetic acid solution; it forms lustrous, orthorhombic crystals which melt at 175° , and are black by reflected, but red by transmitted, light; $a:b:c = 1.45320:1:0.88732$. It is very soluble in alcohol or acetic acid, is dissociated into its components by water and is stable in the air. A dose of 2.5 grams administered internally to a healthy dog of average size had practically no effect; the substance has valuable antiseptic properties, and in some cases may advantageously replace iodoform in the treatment of wounds, ulcers, &c., by reason of its slow liberation of iodine.

A similar compound of paramethoxyphenylsuccinimide,



is also readily obtained; it forms monoclinic crystals resembling the preceding and melting at 150° ; $a:b:c = 1.42472:1:0.91861$. $\beta = 87^\circ 4'$. It is less stable than its homologue, being partially dissociated by acetic acid.

The compound with succinimide $4\text{C}_2\text{H}_4\text{:C}_2\text{O}_2\text{:NH}, \text{KI}, \text{I}_2$, crystallises in large, monoclinic, red tablets, melting at 145° ;

$$a:b:c = 0.99278:1:0.98282. \quad \beta = 74^\circ 16'.$$

The metacatin compound has the composition $2\text{C}_6\text{H}_4(\text{OMe}) \cdot \text{NHAc}, \text{I}_2$, and forms red crystals soluble in acetic acid, or alcohol, but only sparingly so in water.

W. J. P.

Decomposition of Amides and Basic Compounds. By WILLIAM OECHSNER DE CONINCK (*Compt. rend.*, 1896, 122, 34—35).—When treated with Leconte's reagent (sodium hypochlorite) benzamide is slightly decomposed on heating, phthalimide is readily decomposed, and salicylamide begins to decompose at the ordinary temperature. Benzanilide, hydrobenzamide, and azobenzene are not decomposed even on strongly heating; amidoazobenzene is slightly decomposed. Aniline hydrochloride is not decomposed but is converted into coloured products. Orthamidophenol remains practically unaffected even on heating, but the para-derivative is somewhat more readily attacked. The three amidobenzoic acids are decomposed in different degrees and with different velocities. Urethane is decomposed with liberation of nitrogen on gently heating, and ethylic chloride is also formed if the temperature of the liquid is raised rapidly.

C. H. B.

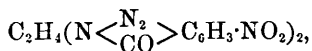
Derivatives of Metanitrororthamidobenzamide and Metanitrororthamidobenzhydrazide. By K. KRATZ (*J. pr. Chem.*, 1896, [2], 53, 210—225; compare *Abstr.*, 1887, 667; 1888, 948).—Meta-nitrobenzazoimide, $\text{NO}_2 \cdot \text{C}_6\text{H}_3 < \begin{array}{c} \text{CO} \cdot \text{NH} \\ | \\ \text{N} = \text{N} \end{array}$ [$\text{NO}_2:\text{CONH}:\text{N}_2 = 5:1:2$],

is prepared by diazotising metanitrorthamidobenzamide; it crystallises in yellowish, silvery, quadratic laminæ, darkens at 178° , and decomposes and melts at 185° ; it dissolves sparingly in cold water, and cold alcohol, but freely in the hot solvents, and in chloroform and glacial acetic acid; ether dissolves it sparingly, benzene not at all; alkalis dissolve it easily, and it is precipitated from the solutions by acids; it is feebly acid to litmus, and explodes when heated on platinum. The sodium salt, $\text{NO}_2 \cdot \text{C}_6\text{H}_3 < \begin{smallmatrix} \text{CO} \cdot \text{N} \cdot \text{N} \text{Na} \\ \text{N} = \text{N} \end{smallmatrix}$, is precipitated by adding ether to mixed alcoholic solutions of the nitrobenzazoimide and sodium; it forms yellowish needles, easily soluble in alcohol and water. The silver salt is described.

Metanitramidobenzomethylamide, $\text{NO}_2 \cdot \text{C}_6\text{H}_3(\text{NH}_2) \cdot \text{CO} \cdot \text{NHMe}$, prepared by the action of methylamine on nitroisatoic acid in water (compare Kolbe, Abstr., 1885, 665), crystallises in yellow needles, melts and partly decomposes at 230 – 231° , and dissolves freely in water, hot glacial acetic acid, and alcohol, sparingly in chloroform, and not at all in benzene. The *methylic* salt of metanitrobenzazoimide may be prepared either by diazotising this methylamide, or by heating sodium metanitrobenzazoimide with methylic iodide; it crystallises in yellow laminæ, melts at 199° and dissolves sparingly in ether, but freely in warm water, warm alcohol, chloroform, glacial acetic acid, and warm methylic alcohol.

Metanitrorthamidobenzethylamide is prepared like the methylamide; it crystallises in long, yellow, brittle needles, becomes brown and melts at 156° , and dissolves sparingly in water and chloroform, more freely in dilute alcohol, and freely in glacial acetic acid. When diazotised, it yields the *ethylic* salt of metanitrorthobenzazoimide; this crystallises in yellowish tables, melts at 105° , and dissolves sparingly in water, but freely in alcohol and glacial acetic acid.

Metanitrorthamidobenzethylenamide, $\text{C}_2\text{H}_4[\text{NH} \cdot \text{CO} \cdot \text{C}_6\text{H}_3(\text{NH}_2) \cdot \text{NO}_2]_2$, from ethylenediamine and nitroisatoic acid, crystallises from hot glacial acetic acid in yellow laminæ, becomes brown at 275° , and melts above 290° . *Ethylenic metanitrorthobenzazoimide*,



is obtained by diazotising the ethylenamide; it crystallises from glacial acetic acid in brown laminæ, and melts above 290° .

Metanitrorthamidobenzanilide, $\text{NO}_2 \cdot \text{C}_6\text{H}_3(\text{NH}_2) \cdot \text{CO} \cdot \text{NHPh}$, from aniline and nitroisatoic acid, forms yellow, silky needles, melts at 203° , and dissolves sparingly in water, alcohol, chloroform, and amyl alcohol, but not at all in ether and benzene; *phenylmetanitrorthamidobenzazoimide* crystallises in yellowish laminæ, and melts at 190° .

The foregoing benzazoimides yield orthamidobenzoic acid when heated with strong caustic potash, metanitrorthochlorobenzoic acid when heated with strong hydrochloric acid at 120 – 130° , and meta-nitrosalicylic acid when heated with dilute sulphuric acid.

Metanitrorthobenzhydrazide, $\text{NO}_2 \cdot \text{C}_6\text{H}_3(\text{NH}_2) \cdot \text{CO} \cdot \text{N}_2\text{H}_3$, is prepared by dissolving hydrazine sulphate with the appropriate quantity of alkali in 10 times its weight of water, and adding nitroisatoic acid in

small portions; it crystallises in yellow needles and decomposes, without melting, between 214° and 218° ; it dissolves easily in alcohol and water, but not in chloroform or ether; glacial acetic acid and nitric acid dissolve it somewhat easily. The *benzylidene* derivative, $\text{NO}_2 \cdot \text{C}_6\text{H}_3(\text{N}:\text{CHPh}) \cdot \text{CO} \cdot \text{NH} \cdot \text{N}:\text{CHPh}$, crystallises in yellow tables, and melts at $224\text{--}225^{\circ}$. When heated with anhydrous formic acid, the hydrazide yields a formyl derivative which is decomposed by hydrolysis into *anhydroformylmetanitroortho-*

amidobenzhydrazide, $\text{NO}_2 \cdot \text{C}_6\text{H}_3 < \begin{array}{c} \text{CO} \cdot \text{N} \cdot \text{NH}_2 \\ | \\ \text{N} = \text{CH} \end{array}$, which crystallises in yellow needles, melts at $170\text{--}171^{\circ}$, dissolves sparingly in chloroform and ether, and easily in hot water and hot alcohol, and has the reactions common to alkaloids. A. G. B.

Derivatives of Orthamidobenzonitrile. By JOHANNES PINNOW and C. SÄMANN (*Ber.*, 1896, **29**, 623—632).—*Orthacetamidobenzonitrile*, obtained by the action of acetic anhydride on amidobenzonitrile, crystallises in long, silky needles, melting at 133° (uncorr.). *Orthobenzamidobenzonitrile* forms needles melting at 216° (uncorr.). *Orthocyanophenylcarbamide* is formed by the action of potassium isocyanate on the hydrochloride of the nitrile; it crystallises in plates, which do not melt below 300° , and is insoluble in all organic solvents except alcohols. *Orthocyanodiphenylcarbamide* is prepared by the combination of the nitrile with phenylcarbimide, and crystallises in plates, which melt at 194° (uncorr.). *Orthocyanothiocarbanilide* is a crystalline powder, which does not melt below 300° . *Orthodicyanothiocarbanilide* crystallises in yellowish plates, which also do not melt below 300° .

Orthamidobenzenylamidoxime, $\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{C}(\text{NH}_2) \cdot \text{N} \cdot \text{OH}$, is obtained by the action of hydroxylamine hydrochloride on a solution of amidobenzonitrile in alcoholic sodium ethoxide; it crystallises in lustrous plates, melts at $84\text{--}85^{\circ}$, and yields a *picrate*, which melts at 182° . The *hydrochloride* is readily soluble in water, and crystallises in slender needles. When it is treated with sodium nitrite, it is converted into *ketodihydrophenotriazinoxime*, $\text{C}_6\text{H}_4 < \begin{array}{c} \text{C}(\text{NOH}) \cdot \text{NH} \\ | \\ \text{N} = \text{N} = \text{N} \end{array}$; this

crystallises from alcohol with 1 mol. of the solvent in slender, light yellow needles, which melt at 181° and lose alcohol when dried. The *hydrochloride* melts at 151° and readily decomposes. The compound is both a weak acid and a weak base. When reduced with stannous chloride and hydrochloric acid, it is converted into *n-dihydro- β -phenotriazine*, $\text{C}_6\text{H}_4 < \begin{array}{c} \text{CH} \cdot \text{NH} \\ | \\ \text{N} - \text{NH} \end{array}$, which crystallises in lustrous plates and melts at 156° . The *hydrochloride* forms thick needles and melts at 169° , whilst the *sulphate* melts at 225° , and the *picrate* at 241° . The base yields a *diacetyl derivative*, which crystallises in needles, melts at 179° , and is decomposed by acids, with re-formation of the original base. The *dibenzoyl derivative* also crystallises in needles and melts at 182° . The base does not give the isonitrile reaction. When *orthamidobenzenylamidoxime* is heated with acetic anhydride, it is con-

verted into *acetorthamidobenzenylazoximethenyl*, $C_{11}H_{11}N_3O_2$, which crystallises in slender needles, melting at 96° . When treated with hydrochloric acid, the corresponding base, *orthamidobenzenylazoximethenyl*, $C_9H_9N_3O$, is formed, which crystallises in short needles and melts at 87° . The *hydrochloride* melts at 178 — 179° . The base readily undergoes the diazo-reaction, and the resulting diazo-salt reacts with β -naphthylamine to form a colouring matter, $C_{12}H_{15}N_5O$, which crystallises in scarlet-red plates and melts at 153 — 154° . When *orthamidobenzonitrile hydrochloride* is treated with sodium nitrite and hydrochloric acid, it is converted into *orthodicyanodiazamidobenzene*, $C_{14}H_9N_5$, which crystallises in small, yellow needles, melting at 133° . When the acid filtrate from this compound is brought into a boiling solution of cupropotassium cyanide, a small quantity of *phthalonitrile*, $C_6H_4(CN)_2$, is formed; this substance crystallises in slender needles, and melts at 141° . A. H.

Halogen Additive Products of the Anilides. By HENRY L. WHEELER and P. T. WALDEN (*Amer. Chem. J.*, 1896, **18**, 85—90).—The substances previously described by Wheeler (this vol., i, 23) as dibromine additive products of metanitracetanilide were mixtures of the perbromides, $(NO_2 \cdot C_6H_4 \cdot NHAc)_2 \cdot HBr, Br_2$ and



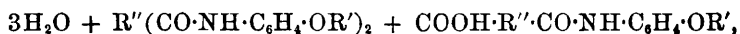
The hydrobromide, $(NO_2 \cdot C_6H_4 \cdot NHAc)_2 \cdot HBr$, from metanitracetanilide, yields a *dibromide*, crystallising in orange-coloured, flat prisms, a *tetrabromide*, forming deep orange prisms, and a *hexabromide*, crystallising in brick-red needles.

The *hydrobromide*, $(C_6H_4 \cdot Br \cdot NHAc)_2 \cdot HBr$, from parabromacetanilide, crystallises in colourless needles; it gives a *dibromide*, forming flat, orange prisms, and a *tetrabromide*, crystallising in deep orange-coloured prisms.

The *hydriodide*, $(NHPhAc)_2 \cdot HI$, from acetanilide, forms shining, colourless scales; it gives a *diiodide*, in ruby-red crystals, and a *tetridide*, crystallising in lustrous, deep, reddish-brown prisms.

These compounds are strictly analogous to the perhaloids $CsBr, Br_2, CsI, I_4$, and NH_4Br, Br_2 . In general, when bromine is mixed with an anilide under conditions which permit of the formation of hydrogen bromide, this acid unites with the anilide to form an ammonium salt, and this salt then unites with bromine. Bromine free from hydrogen bromide has, however, no action on metanitracetanilide or parabromacetanilide. A. E.

Action of Oxalic and Malonic acids on Paramidophenol and its Ethers. By E. CASTELLANETA (*Gazzetta*, 1895, **25**, ii, 527—542).—Piutti has shown (this vol., i, 223) that paramidophenol and phthalic or succinic acid react in molecular proportion, yielding substituted imides; the reaction between oxalic or malonic acid and paramidophenol or its ethers, however, proceeds in accordance with the equation $2R''(COOH)_2 + 3C_6H_4(NH_2) \cdot OR' =$



a substituted diamide and a mono-substituted monamido-acid being produced.

Diparahydroxyphenyloxamide, $C_2O_2(NH \cdot C_6H_4 \cdot OH)_2$, is prepared by melting oxalic acid and the amidophenol together, or by boiling the amidophenol with ethylic oxalate; it forms small crystals, which sublime at 280° . Its *diacetyl* derivative is formed on boiling it with acetic anhydride, and crystallises in scales subliming at 260° .

Diparamethoxyphenyloxamide, $C_2O_2(NH \cdot C_6H_4 \cdot OMe)_2$, from paranisidine and oxalic acid, crystallises in scales melting at 254° . It is accompanied by *paramethoxyphenyloxamic acid*,



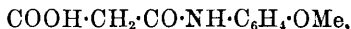
which crystallises in white prisms, melting at $166-167^\circ$; its *ethylic* salt crystallises in colourless scales, melting at 108° .

On extracting with alcohol the product obtained on heating oxalic acid with phenetidine, *diparaethoxyphenyloxamide* remains undissolved, and forms a micro-crystalline powder; it is accompanied by *paraethoxyphenyloxamic acid*, which crystallises in red scales, melting and decomposing at $180-181^\circ$, and gives an *ethylic* salt, crystallising in iridescent scales melting at $110-111^\circ$.

The following compounds are obtained by heating malonic acid, or its *ethylic* salt, with paramidophenol and its alkylic derivatives.

Diparahydroxyphenylmalonamide, $CH_2(CO \cdot NH \cdot C_6H_4 \cdot OH)_2$, crystallises in colourless scales, melting at 235° with decomposition, and yields a crystalline *diacetyl* derivative, melting at 210° .

Diparamethoxyphenylmalonamide forms white needles, melting at $232-233^\circ$; *paramethoxyphenylmalonamic acid*,



crystallises in colourless scales, melting and decomposing at 143° , whilst its *ethylic* salt crystallises in needles, melting at 73° .

Diparaethoxyphenylmalonamide crystallises in colourless needles, melting at $233-234^\circ$; *paraethoxyphenylmalonamic acid* crystallises in colourless scales, melting at 143° with decomposition, and yields an *ethylic* salt, which forms scales, melting at 109° . W. J. P.

Derivatives of Cinnamaldehyde. By MAX SCHOLTZ (*Ber.*, 1896, 29, 613-615).—Cinnamaldehyde condenses with methyl ethyl ketone in the presence of sodium ethoxide; the compound formed, $C_{13}H_{14}O$, melts at $108-110^\circ$, its yellow *oxime* at $142-143^\circ$.

Cinnamylideneacetone, from cinnamaldehyde and acetone, condenses further with benzaldehyde in dilute alcoholic soda solution to a yellow compound, $CHPh \cdot CH \cdot CH \cdot CH \cdot CO \cdot CH \cdot CHPh$, melting at 106° , the yellow *oxime* of which melts at $127-128^\circ$. C. F. B.

Synthesis of Vanillin. By A. FAJANS (*Chem. Centr.*, 1895, ii, 567; from *Ber. Österr. Chem. Ges.*, 1895, 17, 40).—By the action of liquid carbonic anhydride at 120° on sodiorthomethoxyhydroxybenzene, a monocarboxylic acid is formed, but, at 180° , the dicarb-

oxylic acid $[(\text{COOH})_2 : \text{OH} : \text{OMe} = 1 : 5 : 2 : 3]$ is produced, and, when treated with hydrochloric acid under pressure, it yields methylic chloride and isonorhemipinic acid; when heated alone at 277° , vanillic acid $[\text{OH} : \text{OMe} : \text{COOH} = 4 : 3 : 1]$ is produced, and this is converted into vanillin by the action of chloroform and potash.

J. B. T.

Synthesis in the Gentisin Series. By STANISLAUS VON KOSTANECKI and JOSEF TAMBOR (*Monatsh.*, 1895, **16**, 919—925; compare *Abstr.*, 1894, 340).—The monomethyl ether of quinolcarboxylic acid $[\text{OH} : \text{COOH} : \text{OMe} = 1 : 2 : 4]$ is readily obtained from the latter by the action of alkali and methylic iodide. When cautiously distilled with phloroglucinol in presence of acetic anhydride, it yields a yellow sublimate, separable, by means of dilute soda, into two parts. The highly coloured, insoluble portion is the sodium derivative of an acid, which crystallises in broad, yellow needles and melts at 167° ; the latter is identical with the dimethyl ether of trihydroxyxanthone $[\text{OH} : (\text{OMe})_2 = 1 : 3 : 3]$, and is probably produced by the partial methylation of the monomethyl ether by the methylic alcohol formed in the hydrolysis of another portion. Trihydroxyxanthone was detected in the portion of the sublimate soluble in soda, and was accompanied by its monomethyl ether, gentisin, which was isolated by means of its diacetyl derivative.

The above synthesis of gentisin does not afford a complete proof of the constitution of that substance, as the possibility of its production from the trihydroxyxanthone, by methylation, is not excluded.

A. L.

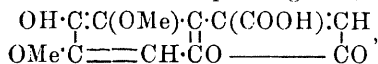
The Behaviour of Alkaline Solutions of Ethylic Formylphenylacetate towards Acids. By WILHELM WISLICENUS (*Ber.*, 1896, **29**, 742—743; compare *Abstr.*, 1895, i, 366).—The liquid isomeride of ethylic formylphenylacetate, which gives a bluish-violet coloration with ferric chloride, is the weaker acid of the two, and has the constitution $\text{OH} \cdot \text{CH} : \text{CPh} \cdot \text{COOEt}$, whilst the solid isomeride has the constitution $\text{CHO} \cdot \text{CHPh} \cdot \text{COOEt}$, and is the stronger acid. Either of the two isomerides can be obtained from the same alkaline solution by varying the treatment adopted. If carbonic anhydride be passed in, the liquid isomeride is precipitated, whilst, if the solution be treated with an excess of sulphuric acid, the solid form is obtained (compare Hantzsch and Schultze, this vol., i, 353). This method appears to be a general one for obtaining isomerides of different acidity.

A. H.

Fraxetin. By PIETRO BIGINELLI (*Gazzetta*, 1895, **25**, ii, 365—373; compare *Abstr.*, 1895, i, 419).—*Ethylic hydroxydimethoxycoumarin- β -carboxylate*,

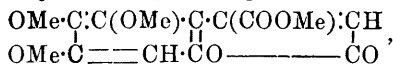
$$\begin{array}{c} \text{OH} \cdot \text{C} : \text{C}(\text{OMe}) \cdot \text{C} : \text{C}(\text{COOEt}) : \text{CH} \\ \text{OMe} \cdot \text{C} = \text{CH} \cdot \text{C} : \text{O} \text{ ————— } \text{CO} \end{array}$$
 is formed on gradually adding a solution of symmetrical dimethoxyquinol in ethylic oxalacetate to concentrated sulphuric acid; on pouring the product on to ice, the salt separates, and is ultimately obtained in prisms melting at $199\text{--}200^\circ$. It is sparingly soluble in water or ether, and dissolves

in alkalis, but not in alkali carbonates. On acidifying its alkali solution with hydrochloric acid, the corresponding *acid*,

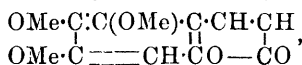


is deposited; it crystallises with $2\text{H}_2\text{O}$ in yellow needles, melting and decomposing at $248\text{--}250^\circ$. These lose their water below 100° , and are soluble in water or alcohol, giving solutions which are yellow when cold, and red when hot. The anhydrous acid is red, but on dissolving it in hot hydrochloric acid and allowing the solution to cool, two *modifications* of the acid, containing H_2O and $\frac{1}{2}\text{H}_2\text{O}$ respectively, are deposited; these crystallise in yellow needles, which do not turn red or lose water on heating, and, when precipitated from their alkali solution by a mineral acid, yield the modification containing $2\text{H}_2\text{O}$.

Methylic trimethoxycoumarin- β -carboxylate,



is obtained by heating a solution of the above acid in methylic alcohol with potash and methylic iodide; after distilling off the solvents, washing with water, and crystallising from alcohol, the salt is obtained in white laminae, melting at $105\text{--}106^\circ$. It is sparingly soluble in alkalis, and, when boiled with potash, undergoes hydrolysis, yielding *trimethoxycoumarin- β -carboxylic acid*, which is precipitated from the solution on adding an acid; it crystallises in yellow needles or scales, melting at 209° , and, like the preceding acid, decomposes above its melting point, with evolution of carbonic anhydride. When distilled with iron powder, it yields *trimethoxycoumarin*,



an isomeride of dimethylfraxetin; this crystallises in white needles melting at $74\text{--}75^\circ$, and is very soluble in alcohol; it is precipitated from its potash or soda solution by carbonic anhydride.

W. J. P.

Optical Activity of Tannin. By HUGO SCHIFF (*Gazzetta*, 1895, 25, ii, 437—442).—The author confirms Gunther's statement (*Ber. d. pharm. Ges.*, 5, 172), that tannin has a small dextrorotation; he therefore proposes to modify the received constitutional formula of gallic and tannic acids, the latter being represented as a ketonic compound, so that they shall be represented as containing asymmetric carbon atoms.

W. J. P.

Ethylic Trinitrophenylmalonate. By C. LORING JACKSON and C. A. SOCH (*Amer. Chem. J.*, 1896, 18, 133—141).—*Ethylic trinitrophenylmalonate* (*picrylmalonate*) is readily obtained by mixing a strong, cold, benzene solution of picryl chloride with an alcoholic solution of ethylic sodiomalonate; it forms long, white, rectangular plates, melting at 58° , and giving pink solutions in most organic solvents. The *sodium derivative*, $\text{C}_6\text{H}_2(\text{NO}_2)_3 \cdot \text{CNa}(\text{COOEt})_2$, forms dark red crystals,

and, when dry, explodes on warming. Its aqueous solution gives red precipitates, with solutions of magnesium, calcium, barium, nickel, lead, and silver salts, and a yellow precipitate with manganese salts.

The *bromo-derivative*, $C_6H_2(NO_2)_3 \cdot CBr(COOEt)_2$, crystallises in white, nearly square, striated plates, melting at $85-86^\circ$; its alcoholic solution has only a faint pink colour. Sodium carbonate has no action, neither has sodium hydroxide in the cold, but on heating, a red solution is obtained, bromine being first removed. *Ethylic bromodinitrophenyl-bromomalonate*, $C_6H_2Br(NO_2)_2 \cdot CBr(COOEt)_2$, was obtained by the action of bromine in excess on a solution of ethylic bromodinitrophenylmalonate (Abstr., 1888, 1091) in glacial acetic acid. It crystallises from alcohol in long, white prisms, melting at $72-73^\circ$. It is insoluble in water, but on long boiling is broken up, the bromine in the side-chain being removed. Strong sodium and ammonium hydroxides have a similar effect on warming, although there is but little action in the cold. A. E.

The Action of Ortho- and Para-nitrobenzylic Chlorides on Ethylic Sodiomalonate and some Analogous Compounds. By ARNOLD REISSERT (*Ber.*, 1896, 29, 633-638).—Orthonitrobenzylic chloride reacts with ethylic sodiomalonate to form ethylic orthodinitrodibenzylmalonate, a portion of the ethylic malonate being regenerated. When twice the molecular proportion of ethylic sodiomalonate is used, however, about three-fifths of the product consists of *ethylic orthonitrobenzylmalonate*. The pure compound is a light red oil, which does not solidify in a freezing mixture, and cannot be distilled without undergoing decomposition. When heated with hydrochloric acid at $140-150^\circ$, it yields orthonitro- β -phenylpropionic acid (Gabriel and Zimmermann, *Ber.*, 13, 1680). Paranitrobenzylic chloride behaves towards ethylic sodiomalonate in a similar manner to the ortho-compound. The mono-substitution derivative has already been described by Lellmann and Schleich (Abstr., 1887, 490). *Ethylic orthoparadinitrodibenzylmalonate* is obtained by the action of orthonitrobenzylic chloride on ethylic paranitrobenzylsodiomalonate in alcoholic solution; it crystallises in white needles, which melt at 103.5° , and, when heated with hydrochloric acid at 180° , yields *orthoparadinitrodibenzylacetic acid*, which was previously obtained by the author as a by-product in the preparation of diorthonitrobenzylacetic acid (Abstr., 1894, i, 626). Orthonitrobenzylic chloride reacts with ethylic sodioacetoacetate to form *ethylic orthodinitrodibenzylacetoacetate*, which crystallises in soft needles melting at 103° . With ethylic cyanoacetate, orthonitrobenzylic chloride yields a mixture of the liquid mono-substitution derivative with *ethylic orthodinitrodibenzylcyanoacetate*, which crystallises in large prisms, and melts at 81° . Orthonitrobenzylic chloride further reacts with ethylic sodiomethanetricarboxylate, forming derivatives of ethylic malonate, a carboxyethyl group being eliminated. A. H.

Sulphoparabromobenzoic Dichloride. By CARL BÖTTINGER (*Chem. Zeit.*, 1895, 19, 1684; compare Abstr., 1878, 729).—The

dichloride of sulphoparabromobenzoic acid may be obtained in a pure state by the following method.

The normal potassium salt of the acid is covered with light petroleum and warmed in a flask with the calculated quantity of powdered phosphorus pentachloride, and the solution of mixed chlorides thus obtained is separated by filtration from potassium chloride, mixed with an equal volume of ether, and repeatedly shaken with water to remove phosphorus oxychloride. On evaporation of the ether, the pure dichloride is deposited in beautiful, oblique, four-sided plates. It melts at 59° , and is readily decomposed by water.

In the preparation of the diethylic salt, *ethylic hydrogen sulphoparabromobenzoate* is also produced, and is found in the mother liquors from the former substance. It is a beautifully crystalline compound melting at 157 – 162° , and is very soluble in water. Both this and the diethylic salt, when heated, yield ethylic parabromobenzoate. As the amidoethylic salt, melting at 128° , formed, together with the corresponding amido-acid, by the action of alcoholic ammonia on the dichloride (*loc. cit.*), gives no trace of ethylic parabromobenzoate on decomposition, it would appear that it is the ethylic salt of parabromobenzamidosulphonic acid. This conclusion is supported by other circumstances.

The author has been unable to obtain a diamide from the above dichloride, as Ullmann stated that he did from the corresponding chloro-compound (Abstr., 1895, i, 181). A. L.

The Action of Phosphorus Pentachloride on Parasulphaminebenzoic acid. By IRA REMSEN, R. N. HARTMAN, and ARTHUR M. MUCKENFUSS (*Amer. Chem. J.*, 1896, **18**, 150–170).—It has been shown that phosphorus pentachloride and benzoic sulphinide, gives orthochlorocyanobenzene (Remsen and Dohme, Abstr., 1889, 992), whilst parasulphaminebenzoic acid yields parachlorocyanobenzene. A further investigation of the latter reaction has now been made, and shows that, below 70° , *phosphochloroparasulphaminebenzoic chloride*, $\text{COCl}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2\cdot\text{NPCl}_2$, is formed; at 146 – 200° this gives off phosphoric oxychloride, leaving *paracyanobenzenesulphonic chloride*, $\text{CN}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2\text{Cl}$; and at 205° the latter breaks up into SO_2 and parachlorocyanobenzene, $\text{C}_6\text{H}_4\cdot\text{Cl}\cdot\text{CN}$.

Phosphochloroparasulphaminebenzoic chloride crystallises in transparent prisms, which quickly turn white on exposure to air, and absorb moisture eagerly, giving off hydrogen chloride. It melts at 82° , and dissolves in warm water, forming parasulphaminebenzoic acid.

Paracyanobenzenesulphonic chloride crystallises in large, rhombic, transparent prisms, melts at 111 – 112° , and sublimes in rough, white needles. With aqueous ammonia, an amide is formed which, on treatment with alkalis, or on heating with water in a sealed tube, is converted into parasulphaminebenzoic acid.

When the chloride is heated with water at 200° in a sealed tube, it yields the acid ammonium salt of parasulphobenzoic acid, which was identified by transforming it into the barium salt (Remsen, this Journal, 1876, i, 257). On simply boiling with water, paracyanobenzenesulphonic chloride is converted into the corresponding acid,

$\text{CN}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_3\text{H}$ [1 : 4], which separates from the concentrated aqueous solution in small, prismatic crystals. Owing to its great solubility, it could not be purified sufficiently for analysis. The *barium* and *potassium* salts are described. *Paracyanobenzenesulphonamide*, $\text{CN}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2\text{NH}_2$, crystallises from hot water in long, lustrous prisms melting at $168\text{--}169^\circ$. *Paracyanobenzenesulphonanilide*,



crystallises from alcohol in long, prismatic plates, and from benzene in fine, flat, satiny needles melting at 112° . Alkalis decompose it, on boiling, with evolution of ammonia, and from the alkaline solution acids precipitate *parasulphanilidobenzoic acid* as a white, flocculent mass. This may be crystallised from alcohol in feathery plates melting and partially decomposing at $252\text{--}253^\circ$. The *barium* salt, with $5\text{H}_2\text{O}$, and the *potassium* salt, with $2\text{H}_2\text{O}$, are described.

Paracyanobenzenesulphorthotoluidide, $\text{CN}\cdot\text{C}_6\text{H}_3\cdot\text{SO}_2\cdot\text{NH}\cdot\text{C}_7\text{H}_7$, forms prisms melting at $122\text{--}123^\circ$. *Orthotoluidoparasulphobenzoic acid*, $\text{COOH}\cdot\text{C}_6\text{H}_3\cdot\text{SO}_2\cdot\text{NH}\cdot\text{C}_7\text{H}_7$, resembles the anilido-acid, and crystallises from alcohol in white, flat needles melting and decomposing at $246\text{--}247^\circ$. The *barium* salt crystallises, with $5\text{H}_2\text{O}$, in minute, white plates, or with H_2O in larger prismatic plates. *Paracyanobenzene-sulphometatoluidide* forms white prisms melting at 128° . *Metatoluidoparasulphobenzoic acid* crystallises from alcohol in white, shining plates or leaflets melting at $241\text{--}242^\circ$; the *barium* salt, with $5\text{H}_2\text{O}$, forms long prisms, or with $3\text{H}_2\text{O}$, lustrous, prismatic plates. *Paracyanobenzenesulphoparatoluidide* crystallises in rhombic prisms melting at $151\text{--}152^\circ$, and dissolves unchanged in alkalis, but, on heating the solution, *paratoluidoparasulphobenzoic acid* is obtained; this forms beautiful, white plates or leaflets melting and decomposing at $282\text{--}283^\circ$. The *barium* salt, with H_2O , crystallises in small, white prisms.

On heating a mixture of parasulphaminebenzoic acid and phosphorus pentachloride, *parachlorcyanobenzene* distils as an oil which soon solidifies. It is deposited from hot alcohol in long, prismatic needles which gradually dissolve on standing, and are replaced by new crystals much shorter and thicker than the first. The melting point is $93\text{--}94^\circ$. A. E.

Dissociation of Diazosulphonates. By EUGEN BAMBERGER (*Ber.*, 1896, **29**, 608—610).—Hantzsch has calculated his cryoscopic results (*Abstr.*, 1895, i, 664) wrongly. Properly calculated, they lead to conclusions the opposite of those which he states. The anti-salt exhibits *increasing*, and not decreasing, dissociation with increase of concentration. And, further, the iso- (anti-) salt appears more dissociated, hydrolytically, than is the normal (syn-) salt—which is contrary to experience. C. F. B.

The Stereoisomeric Salts of Diazosulphanilic acid. By DIMITER GERILOWSKI and ARTHUR R. HANTZSCH (*Ber.*, 1896, **29**, 743—755; compare *Abstr.*, 1895, i, 664).—The electrical conductivity of solu-

tions of the anti-sodium salt prepared from paradiazosulphanilic acid show that at 0° , $\mu = 80.2$ ($v = 32$), 97.4 ($v = 1024$), the increase in μ between the values $v = 32$ and $v = 1024$ being, therefore, 17.2 . This agrees well with the numbers obtained for other sodium salts of dibasic acids which are not hydrolysed by the water of dissolution; sodium succinate, for example, shows an increase of 18.76 at the same temperature. The syn-salt gives the values $\mu = 81$ ($v = 32$), and $\mu = 112$ ($v = 1024$); the difference in this case being 31 . This shows that the syn-salt, which possesses the normal structure, is hydrolysed to a larger extent than the anti-salt; so that the normal diazo-group must be considered to be of a less acid character than the iso-group. The dissociation of the two salts undergoes almost the same diminution when a molecule of caustic soda is added. These results are considered by the authors to prove that the two salts have a similar constitution, and that the normal salt cannot have the constitution $\text{NaSO}_3 \cdot \text{C}_6\text{H}_4 \cdot \text{N}(\text{ONa}) \cdot \text{N}$, since, in that case, it would be almost as completely dissociated as caustic soda, for which $\mu = 128$ when $v = 32$.

The change from diazonium compound to syn-diazo-compound, which occurs when diazoniumsulphanilic acid is dissolved in caustic soda, appears to take place with great rapidity, as the solution shows the conductivity of the syn-salt as soon as it is prepared. The reverse change takes place very rapidly when a mineral acid is added to the alkaline solution. The change from syn- to anti-salt occurs extremely slowly at 0° , and does not interfere with the determination of the conductivity.

A comparison of the oximes shows that the syn-oxime is a stronger acid than the anti-oxime.

A. H.

Synthesis of Diphenylene Ketone and its Derivatives. By WILHELM STAEDEL (*Ber.*, 1896, **29**, 615).—Syntheses of this kind, which Pschorr proposes to attempt (this vol., i, 303), have already been carried out by the author (*Abstr.*, 1895, i, 147, 233) and others

C. F. B.

Action of Sulphuric acid on Benzilic acid. By HEINRICH C. KLINGER and CARL LONNES (*Ber.*, 1896, **29**, 734—741; compare *Abstr.*, 1889, 885).—Four products are formed by the action of cold concentrated sulphuric acid on benzilic (diphenylglycollic) acid or its air-dried potassium salt, a mixture of these being precipitated when the product of the action is diluted with ice. When the drained mass is dissolved in benzene, and this solution shaken with potash, a sulphonic acid is dissolved out together with an acid of the formula $\text{C}_{27}\text{H}_{20}\text{O}_3$; the potassium salt of a third acid, $\text{C}_{40}\text{H}_{30}\text{O}_4$, separates in needles, whilst the benzene solution retains the fourth substance, diphenyldiphenylenesuccinic anhydride. The acid, $\text{C}_{40}\text{H}_{30}\text{O}_4$, melts at 208 — 210° , and forms a *potassium salt*, which is almost insoluble in water; the *methylic salt* melts at 208 — 209° . When the acid is reduced with hydriodic acid at 160 — 170° , it yields diphenyleneacetic acid and diphenylmethane, and has, therefore, probably the constitution $\begin{matrix} \text{C}_6\text{H}_4 \\ | \\ \text{C}_6\text{H}_4 \end{matrix} > \text{C}(\text{COOH}) \cdot \text{C}_{26}\text{H}_{21}\text{O}_2$. On oxidation with chromic

acid, the acid is converted into *tetraphenyldiphenylenetrioxymethylene*, $\begin{matrix} \text{C}_6\text{H}_4 \\ | \\ \text{C}_6\text{H}_4 \end{matrix} > \text{C} \begin{matrix} \text{O} \cdot \text{CPh}_2 \\ \text{O} \cdot \text{CPh}_2 \end{matrix} > \text{O}$; this crystallises in plates which have a golden lustre, and melt at 205—206°. When its solution in acetic acid is boiled with hydriodic acid, it yields *tetraphenyldiphenylenepropylene oxide*, $\text{C}_{39}\text{H}_{28}\text{O}$, which crystallises in well-developed yellow prisms, melts at 202—203°, and is re-converted into the trioxymethylene compound by chromic acid. Complete reduction converts the substance into diphenylmethane and fluorene. Hydriodic acid at 110—120°, however, converts it into *tetraphenyldiphenylenepropane*, $\begin{matrix} \text{C}_6\text{H}_4 \\ | \\ \text{C}_6\text{H}_4 \end{matrix} > \text{CH} \cdot \text{CPh}_2 \cdot \text{CHPh}_2$, which is also formed in small quantity when the acid $\text{C}_{40}\text{H}_{30}\text{O}_4$ is distilled with soda-lime, and when the propylene oxide is treated with zinc dust and acetic acid, in the latter case it is accompanied by two compounds, of the formula $\text{C}_{39}\text{H}_{30}\text{O}$, melting at 186° and 223° respectively. It crystallises in long, white needles, and melts at 205°. When the potassium salt of the acid is heated at 120—150° with an indifferent solvent, it yields potassium carbonate and a substance of the formula $\text{C}_{39}\text{H}_{30}\text{O}_2$, which crystallises well, melts at 220° and is converted by oxidation into the trioxymethylene compound.

Diphenyldiphenylenesuccinic anhydride, $\begin{matrix} \text{C}_{12}\text{H}_8 \cdot \text{C} & \text{---} & \text{CO} \\ | & & | \\ \text{CPh}_2 & & \text{CO} \end{matrix} > \text{O}$, forms well-developed crystals melting at 256°. Its solution in alcoholic potash deposits the corresponding acid on acidification, but this passes into the anhydride on drying. Hydriodic acid converts it into diphenyleneacetic and diphenylacetic acids. When the anhydride is heated with aqueous potash at 150° it forms *diphenyldiphenylenepropionic acid*, $\text{C}_{12}\text{H}_8 \cdot \text{CH} \cdot \text{CPh}_2 \cdot \text{COOH}$, which crystallises in white plates, and melts and decomposes at 239°, whilst, on reduction, it yields *diphenyldiphenylenethane*, $\text{C}_{12}\text{H}_8 \cdot \text{CH} \cdot \text{CHPh}_2$, which forms white needles melting at 217°. On oxidation, the acid is converted into benzophenone fluorene ketone and diphenyldiphenylenethylene, $\text{C}_{12}\text{H}_8 \cdot \text{C} \cdot \text{CPh}_2$, which melts at 225—226°. This hydrocarbon is colourless, but yields deep, yellow-coloured solutions, and is identical with the hydrocarbon obtained from benzophenone chloride and fluorene (Kaufmann, this vol., i, 242).

The acid $\text{C}_{27}\text{H}_{20}\text{O}_3$ is an amorphous, white mass, and in alkaline solution readily oxidises on exposure to the air, forming a substance of the formula $\text{C}_{26}\text{H}_{18}\text{O}_2$; this crystallises in plates with a golden lustre, and melts at 175°. This is unaffected by most reagents, but is reduced by hydriodic acid to fluorene and diphenylmethane; on moderate reduction, it forms a compound, $\text{C}_{26}\text{H}_{18}\text{O}$, which is also yellow, and melts at 157°.

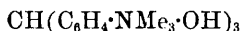
When it is reduced, it yields a hydrocarbon ($\text{C}_{13}\text{H}_{10}$)_n, which melts at 149—150°, and is perhaps *as*-diphenyldiphenylenethane.

The molecular weights of the various compounds described were, almost without exception, determined by the cryoscopic method.

A. H.

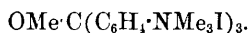
Acid Rosanilines. By MAURICE PRUD'HOMME (*Bull. Soc. Chim.*, 1896, [3], **13**, 581—583).—A controversial reply to Rosenstiehl (*Abstr.*, 1895, i, 667). JN. W.

Ammoniated Derivatives of Hexamethyltriamidotriphenylmethane. By AUGUSTE ROSENSTIEHL (*Bull. Soc. Chim.*, 1896, [3], **13**, 546—581; compare *Abstr.*, 1895, i, 377, 476).—Hexamethyltriamidotriphenylmethane, $\text{CH}(\text{C}_6\text{H}_4\cdot\text{NMe}_2)_3$, combines readily with methylic iodide in the cold to form a *trimethiodide*, $\text{CH}(\text{C}_6\text{H}_4\cdot\text{NMe}_3\text{I})_3$, crystallising in colourless needles, and melting and decomposing at 188° ; it is rather unstable, gradually losing methylic iodide when kept. The methiodide is converted by caustic alkalis, or better, by moist silver oxide, into the corresponding *hydroxide*,



which, like the other compounds of this type, could not be crystallised. Alcoholic soda simply removes methylic iodide, the original compound being formed again. It is probable that an intermediate leuco-base is formed, as at a certain stage in the action, a green dye is produced by the action of lead oxide and acetic acid, distinct from the violet dye produced under the same conditions from the original substance. It is noteworthy that the corresponding carbinol derivatives yield colouring matters with acetic acid alone, without the aid of oxidising agents.

The carbinol may conceivably act with methylic iodide in two ways, namely, as a tertiary amine or as a carbinol, and it is probable that the action proceeds in both directions, as a considerable quantity of a violet colouring matter, $\text{Cl}(\text{C}_6\text{H}_4\cdot\text{NMe}_2)_3$, is formed, involving the production of an equivalent amount of the compound

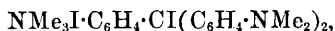


The main product of the action of methylic iodide is, however, the simple additive product $\text{OH}\cdot\text{C}(\text{C}_6\text{H}_4\cdot\text{NMe}_3\text{I})_3\cdot 3\text{H}_2\text{O}$. This may be partially dehydrated by heating in methylic iodide vapour at 150° , but under ordinary conditions it loses methylic iodide before the water of hydration is expelled. *Hexamethyltriamidotriphenylcarbinol trimethiodide* forms colourless crystals, and is much more soluble in water than the corresponding hydrocarbon derivative. It is partially converted by caustic alkalis, and completely by moist silver oxide, into the corresponding *hydroxide*, $\text{OH}\cdot\text{C}(\text{C}_6\text{H}_4\cdot\text{NMe}_3\cdot\text{OH})_3$, which forms a transparent, non-crystalline, almost colourless mass, having a strong alkaline reaction. Its reactions are similar to those of the tetralkylammonium hydroxides.

Methoxyhexamethyltriamidotriphenylmethane, $\text{OMe}\cdot\text{C}(\text{C}_6\text{H}_4\cdot\text{NMe}_2)_3$, is formed by the action of caustic soda on a methyl alcoholic solution of the corresponding hydrochloride, "crystal violet"; it is an iridescent, crystalline powder melting and decomposing at 165° . The corresponding *ethoxy-compound* melts at 143° . The *amyloxy-compound* was also prepared. The *trimethiodide* of the methoxy-compound, with $3\text{H}_2\text{O}$, is formed with development of heat, by the direct addition of methylic iodide to the methylic derivative of the carbinol. It is a colourless sub-

stance which may be partially dehydrated in methylic iodide vapour at 150° . The corresponding derivative of the ethoxy-compound crystallises in large, anhydrous prisms, which are heavy and opaque. The *amyloxy*-compound is pulverulent, and very freely soluble in water.

The green dyes obtained from the products intermediate between the trimethiodides and the dimethylamido-compounds, by oxidising them with lead oxide and acetic acid, could not be purified, but their identity was established by synthesis. The *methiodide* of the methoxy-compound, $\text{NMe}_3\text{I}\cdot\text{C}_6\text{H}_4\cdot\text{C}(\text{OMe})(\text{C}_6\text{H}_4\cdot\text{NMe}_2)_2$, the principal product of the direct addition of methylic iodide, crystallises from methylic alcohol in colourless needles, and melts and decomposes at 195° . It is converted by acids into the corresponding *iodide*,



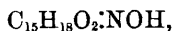
a green dye crystallising in large needles, having a metallic lustre. When heated, this loses methylic iodide, and is converted into the original violet dye, but is converted by moist silver oxide into the corresponding *dihydroxy*-compound, a yellowish alkaline substance. The intermediate compound, $\text{NMe}_3\text{I}\cdot\text{C}_6\text{H}_4\cdot\text{C}(\text{OH})(\text{C}_6\text{H}_4\cdot\text{NMe}_2)_2$, is similar.

JN. W.

Santonin acid and its Derivatives. By LUIGI FRANCESCONI (*Gazzetta*, 1895, 25, ii, 461—478; compare *Abstr.*, 1894, i, 204).—*Monacetylsantonin acid*, $\text{C}_{15}\text{H}_{19}\text{O}_4\text{Ac}$, is obtained by boiling santonin acid with acetic anhydride, treating with sodium carbonate, and extracting the solution with ether; it crystallises in long needles melting at 197 — 198° , is soluble in alcohol or acetic anhydride, and is not hydrolysed by boiling water, but dissolves in alcoholic potash yielding a solution from which hydrochloric acid precipitates santonin acid.

Diacylsantonin acid, $\text{C}_{15}\text{H}_{18}\text{O}_4\text{Ac}_2$, is prepared by boiling santonin acid with acetic anhydride and sodium acetate, the product being treated with sodium carbonate and extracted with ether; it crystallises in transparent needles, melts at 207° , and is soluble in alcohol and acetic anhydride. Although not hydrolysed by boiling water, it is by alcoholic potash, and from the solution hydrochloric acid precipitates metasantonin acid. Neither of these acetyl derivatives reacts with hydroxylamine.

Metasantonin (isosantonin), obtained by Valente's process (*Real. Accad. Lincei*, [3], 3, 242) of heating santonin acid with sulphuric acid, melts at 137 — 138° , and dissolves readily in fuming hydrochloric acid, forming a compound with it from which metasantonin is again obtained on treatment with water. When boiled with hydroxylamine and calcium carbonate, it yields *metasantoninoxime*,



which crystallises in long needles melting at 220° , and in a 1.6776 per cent. alcoholic solution has the specific rotation at 25° of $[\alpha]_D = -377^{\circ}$; it is readily decomposed on boiling with dilute hydrochloric acid, yielding metasantonin. The oxime is easily reduced by zinc

dust and hydrochloric acid with formation of *hydrometasantonin*, $C_{15}H_{20}O_3$, which crystallises from alcohol or acetic acid in brilliant needles melting at $181-182^\circ$; and may also be prepared by reducing metasantonin with zinc dust and hydrochloric acid; it does not react with acetic chloride, or with acetic anhydride and sodium acetate, and in a 2.8916 per cent. chloroform solution at 25° it has the specific rotation $[\alpha]_D = -102.6^\circ$. *Hydrometasantoninoxime*, $C_{15}H_{20}O_2 \cdot NOH$, crystallises in small opaque needles, which turn brown at 190° and melt at 196° ; in a 1.7924 per cent. alcoholic solution it has the specific rotation $[\alpha]_D = -239^\circ$.

Metasantoninic acid is best prepared by heating santonic acid dissolved in acetic acid in a closed tube at 300° for 7—8 hours. Methylic metasantonate, when heated with hydroxylamine hydrochloride and calcium carbonate, yields the corresponding *oxime*, $C_{16}H_{22}O_5 \cdot NOH$; this crystallises in large tablets melting at 171° , is readily hydrolysed by cold hydrochloric acid, and in a 2.9712 per cent. alcoholic solution at 25° has the specific rotation $[\alpha]_D = -175^\circ$. The *oxime* of ethylic metasantonate obtained in the same way, resembles the methylic compound, and melts at 166° , but the *oxime* of metasantoninic acid can only be obtained crystalline with difficulty.

Acetylmetasantoninic acid, $C_{17}H_{22}O_6$, is prepared by boiling a solution of metasantoninic acid in acetic anhydride; it is a white crystalline substance melting at $202-203^\circ$, is not hydrolysed by boiling water, and yields metasantoninic acid with alcoholic potash. Ethylic metasantonate remains unaltered when boiled with acetic anhydride.

The author gives an improved process for preparing santonide; when dissolved in fuming hydrochloric acid, it is converted into *isosantoninic acid*, $C_{15}H_{20}O_4$, which forms transparent crystals melting at 152° , and in a 3.3828 per cent. chloroform solution at 25° has the specific rotation $[\alpha]_D = -73.92^\circ$. Its *barium*, *silver*, *copper*, and *lead* salts are sparingly soluble or insoluble in water. The *methylic* salt, $C_{15}H_{19}MeO_4$, separates from ether in large, porcelain-like crystals melting at $69-70^\circ$, and is very soluble in ether, alcohol, or ethylic acetate; it is not acted on by acetic anhydride, and in a 2.2916 per cent. chloroform solution at 27° it has the specific rotation $[\alpha]_D = -50.2^\circ$. The *ethylic* salt melts at 76° , and is similar in appearance and properties. Isosantoninic acid does not yield an acetyl derivative with acetic anhydride, but is converted into its anhydride, santonide; neither the acid nor its alkyl salts combine with hydroxylamine.

W. J. P.

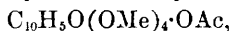
Thio-derivatives of Phenols. By ARNOLD VOSWINKEL (*Chem. Centr.*, 1895, i, 1060; from *Pharm. Zeit.*, 1895, **40**, 241—242; compare Tassinari, *Abstr.*, 1891, 186).—The product of the action of thionyl chloride on β -naphthol was dissolved in potash, and then treated with hydrochloric acid, when the original product, β -thio-naphthol, separated out. It therefore follows that this compound is β -thionaphthol, and not β -naphthol sulphite, which would, under the given treatment, yield β -naphthol and potassium sulphite. The following thiophenols have been prepared. Thiophenol, m. p. 148° (Tassinari gives 150°), *thio- α -naphthol*, *thio-orthocresol*, and *thioparacresol*; *methylic thiosalicylate*, *thioguaiacol*, *thioeugenol*, which are

liquids; *thioresorcinol*, m. p. 120° , *thiothymol*, m. p. 146° , *thiomenthol*, m. p. 52° . J. J. S.

Hæmatoxylin and Brazilin. III. By JOSEF HERZIG (*Monatsh.*, 16, 906—918; compare *Abstr.*, 1893, i, 426; 1894, i, 341).—When acetyltrimethylhæmatoxylin is warmed on the water bath with one-half its weight of chromic acid in glacial acetic acid solution, an *acetyl* compound is produced, which, after hydrolysis, is completely soluble in alkalis. After dissolving it in the latter, and reprecipitating by carbonic anhydride, it may be separated by means of alcohol into two portions; the crystalline portion, which is but sparingly soluble in alcohol, decomposes on exposure to the air, and on analysis gives numbers agreeing with the formula of *tetramethyldehydrohæmatoxylin*, $C_{16}H_{15}O(OMe)_4.OH$. It melts at $202-206^{\circ}$.

Pentamethyldehydrohæmatoxylin, $C_{10}H_5O(OMe)_5$, is formed on treating the preceding compound with alkali and methylic iodide. It is quite stable, and may readily be obtained in a pure state; it is only very sparingly soluble in alcohol, separating from the solution in beautiful white needles, which melt at $160-163^{\circ}$. It appears to react with bromine.

Tetramethyldehydrohæmatoxylin, when heated with acetic anhydride and sodium acetate, yields an *acetyl* derivative,



which is slightly soluble in alcohol, crystallises in white needles, and melts at $190-192^{\circ}$.

The above compounds contain four atoms of hydrogen less than the corresponding hæmatoxylin derivatives.

Hæmatoxylin, when fused with caustic potash, yields almost at once a black substance, insoluble in all media with the exception of alkalis; it is not affected when kept in fusion with potash at $300-350^{\circ}$ during two days.

Trimethyldehydrobrazilin, $C_{10}H_5O(OMe)_3.OH$, is formed by the oxidation of trimethylacetylrazilin and hydrolysis of the resulting acetyl derivative; it is even more unstable than the hæmatoxylin derivative above mentioned, and was not obtained pure. On acetylation, it yields an *acetyl* derivative, $C_{16}H_5O(OMe)_3.OAc$, which separates from alcohol, in which it is but slightly soluble, in white, shimmering leaflets, and melts at $174-176^{\circ}$.

Tetramethyldehydrobrazilin, $C_{16}H_5O(OMe)_4$, produced by the methylation of the corresponding trimethyl derivative, is sparingly soluble in all media, and has not been obtained with any constant melting point. The specimen analysed melted at $136-155^{\circ}$.

The oils obtained at the same time as tetramethyldehydrohæmatoxylin and trimethyldehydrobrazilin appear to contain isomerides of these substances, and, on methylation, yield crystalline compounds having the compositions of pentamethyldehydrohæmatoxylin and tetramethyldehydrobrazilin respectively. A. L.

Russian Oil of Aniseed. By GEORGES BOUCHARDAT and TARDY (*Compt. rend.*, 1896, 122, 198—201).—Russian oil of aniseed con-

sists mainly of anethoil, but also contains small quantities of anisic camphor, anisaldehyde, which boils at $245-248^{\circ}$, sp. gr. = 1.141 at 0° , and a substance which has the composition $C_{10}H_{10}O_2$ or $C_{10}H_{12}O_2$, yields anisic and acetic acids on oxidation, and seems to be anisic ketone (b. p. about 263° , sp. gr. = 1.095 at 0°). Minute quantities of anisic acid are also present.

C. H. B.

Oil of Scotch Fir (*Pinus sylvestris*) and other Pine Oils.

By JOHN C. UMNEY (*Pharm. J. Trans.*, 1895, **55**, 161 and 542).—The oil of *Pinus sylvestris* may show differences of rotation, depending on the season of the year when the materials are gathered or on the conditions of climate and soil. These differences in rotation should not exceed 20° in either direction in a 100-mm. tube. The sp. gr. of the oil should not fall below 0.880 at 15° . A very considerable part of the oil should distil above 185° , and not more than 15 per cent. below 170° .

The oil of *Abies canadensis* showed a sp. gr. of 0.9026 at 15° , and a rotation of -25° in a 100-mm. tube. This oil contained about 29.4 per cent. of bornylic acetate, and gave no indication of sylvestrene by Wallach's reaction.

The oil of *Abies excelsa* is that commonly sold as pine-needle oil, but it is easily distinguished by its lower specific gravity and its marked levorotation of -70° . Oil of *Picea vulgaris* had a sp. gr. = 0.8806 at 15° , and a rotation of -37° in a 100-mm. tube. Oil of *Pinus pumilio* had a sp. gr. = $0.865-0.870$, and a rotation of -7.5° .

R. R.

Oxidation of Pinene. By GEORG WAGNER and GEORG ERTSCHIKOWSKY (*Ber.*, 1896, **29**, 881—885; compare *Abstr.*, 1894, i, 610).—*Pinononic acid*, $C_9H_{14}O_3$, obtained by oxidising French turpentine with a 1 per cent. solution of potassium permanganate at 0° , crystallises from chloroform in transparent rhombohedra and prisms; it dissolves sparingly in cold water, and is insoluble in petroleum. The acid melts at $128-129^{\circ}$, and the *oxime*, which crystallises from water in plates, melts at $178-180^{\circ}$; a second *acid*, arising from the oxidation of pinene, and resembling cotton wool when crystallised from water, melts at $103-104^{\circ}$, and does not combine with hydroxylamine. Pinononic acid is also formed when the keto-alcohol, $C_{10}H_{16}O_2$ (*loc. cit.*), remains in contact with silver oxide for several weeks; alkali hypobromite converts it into the *acid*, $C_8H_{12}O_4$, which crystallises in transparent prisms and melts at $173-174^{\circ}$; bromoform and carbon tetrabromide being produced at the same time.

Among the neutral products of oxidation of French turpentine is an aldehyde which, on exposure to air, yields an acid resembling the camphenylic acid (m. p. $171.5-172.5^{\circ}$) obtained from camphene.

The authors point out that the production of pinononic acid is fresh evidence in favour of Wagner's formula for pinene, already supported by von Baeyer (this vol., i, 245) on obtaining α -pinonic acid from the hydrocarbon.

M. O. F.

Constitution of Pinene. By GEORG WAGNER and ALEXANDER GINZBERG (*Ber.*, 1896, **29**, 886—890; compare foregoing abstract).—The statement of Wheeler relating to the behaviour of pinene towards

hypochlorous acid has been confirmed, a compound, $C_{10}H_{17}O_2Cl$, being obtained in large, transparent, rhombic crystals; two modifications are produced, melting at $131-133^\circ$ and $105-107^\circ$ respectively, the former being more sparingly soluble in a mixture of ether and methylic alcohol. The compound is probably a monochlorhydrin of pinolglycol, the latter substance being produced along with it. Hypobromous acid converts pinene into Wallach's pinene bromide, which melts at $169-170^\circ$ (Abstr., 1891, 1241).

The authors adhere to Wagner's formula for pinene.

M. O. F.

The Pinene Problem. By FERDINAND TIEMANN (*Ber.*, 1896, **29**, 890—892; compare the two foregoing abstracts).—A polemical paper, in which the author criticises Wagner's views, and advocates the formula for pinene put forward by Semmler and himself.

M. O. F.

Constitution of Menthene and its Products of Oxidation.

By ST. TOLLOCZKO (*Chem. Centr.*, 1895, **1**, 543—544; from *Anz. Akad. Wiss., Krakau*, 1894, 267).—By the oxidation of menthene, $C_{10}H_{18}$, with potassium permanganate, the author has obtained *menthene glycol*, $C_{10}H_{18}(OH)_2$, in two physically isomeric forms, one of which is a liquid and the other a crystalline solid. A ketone-alcohol, $C_{10}H_{17}O \cdot OH$, which is a liquid, $[\alpha]_D = -1^\circ 35'$, $K_{13.5} = 104.5-105.5^\circ$, and various acid products formed by the decomposition of the original menthene molecule were also obtained. The representation of menthene by the formula $CHMe < \begin{smallmatrix} CH_2 \cdot CH_2 \\ CH_2 \cdot CH \end{smallmatrix} > CPr^2$, agrees with these facts.

Menthol, when treated with sulphuric acid, yields a hydrocarbon, *menthane*, $C_{10}H_{20}$, having the properties of a polymethylene derivative. Other products are also formed; among these the author has found cymenesulphonic acid and a *hydrocarbon*, $C_{20}H_{36}$.

J. J. S.

Camphene Bromide. By ALBERT REYCHLER (*Ber.*, 1896, **29**, 900—901; compare Jünger and Klages, this vol., i, 313).—When camphene is brominated in a mixture of ether and alcohol, and the product, after precipitation with water, submitted to distillation in an atmosphere of steam, an oil is obtained, which probably has the formula $C_{10}H_{15}Br$; *camphene bromide*, $C_{10}H_{16}Br_2$, which remains in the distilling flask, crystallises from alcohol in colourless, doubly refractive prisms, melting at 90° . The derivative is also formed when the bromination is conducted at -10° , light petroleum being employed as the medium.

M. O. F.

Geraniol and Rhodinol. By JULIUS BERTRAM and EDUARD GILDEMEISTER (*J. pr. Chem.*, 1896, [2], **53**, 225—237; compare Abstr., 1894, i, 253).—The authors review the history of geraniol, and summarise the present knowledge of this alcohol as follows: (1) The alcoholic portion (b. p. about 230°) of Indian geranium oil (*Andropogon Schænanthus*), of citronella oil (*Andropogon Nardus*), and of rose oil, consists exclusively or nearly so, of geraniol; the same is true of Barbier's licarhodol (Abstr., 1893, i, 544). (2) The essential oil of the pelargoniums (the French, African, and Reunion geranium oil)

contains a considerable proportion of geraniol in that part of the alcoholic constituent which boils at 225—230°; but there is also present a second alcohol, which has not yet been obtained in a pure condition, and whose properties and composition have, in consequence, not been determined. This second alcohol appears, however, to be differentiated from geraniol by its lower boiling point, its lower specific gravity, and its behaviour towards hydrogen chloride and towards calcium chloride, with which it forms no solid compound. According to Barbier and Bouveault (*Abstr.*, 1895, i, 4), the new alcohol yields α -methyladipic acid by energetic oxidation, whilst geraniol yields terebic acid.

The work of Erdmann and Huth (this vol., i, 198) is next unfavourably criticised; it is complained that these authors have obscured the issue by substituting the name rhodinol for geraniol.

Geraniol, prepared from the calcium chloride compound, was shaken with not quite anhydrous formic acid at the ordinary temperature, the product, after being saponified, was distilled, and the 175—185° fraction was shaken with chromic acid mixture (Baeyer, *Abstr.*, 1894, i, 297); the oil which was then distilled over with steam no longer gave any reaction with chromic acid, and, when brominated, yielded dipentene tetrabromide, showing that dipentene, besides terpinene, is obtained by the action of formic acid on geraniol.

A. G. B.

The Alleged Identity of Reuniol, Rhodinol, and Geraniol.

By ALBERT HESSE (*J. pr. Chem.*, 1896, [2], 53, 238—241; compare *Abstr.*, 1895, i, 186).—A reply to Erdmann and Huth (this vol., i, 198). The author maintains the individuality of renniol, and points out that he has already prepared and patented many ethereal salts such as Erdmann and Huth claim to have discovered.

A. G. B.

Method of purifying Alcohols. By FERDINAND TIEMANN and PAUL KRÜGER (*Ber.*, 1896, 29, 901—903).—Many alcohols of the terpene series undergo change when submitted to the influence of acidic agents or the prolonged application of heat, and the authors accordingly employ a method of purifying alcohols which is independent of these conditions. In purifying linalol, for instance, sodium is dissolved in the alcohol, which is then distilled under reduced pressure from the sodium derivative; the latter is suspended in dry ether, and treated with succinic, or, preferably, phthalic anhydride, remaining in contact with it during several days. On agitating [the liquid with water, the linalolic sodium phthalate is dissolved, and after being repeatedly washed with ether, the solution is acidified and again extracted with that agent; the ethereal salt is then hydrolysed with alcoholic potash, and the pure alcohol is obtained from this liquid by precipitation with water. The yield amounts to 40—60 per cent. of the crude material.

M. O. F.

Compounds of the Citronellal Series. By FERDINAND TIEMANN and R. SCHMIDT (*Ber.*, 1896, 29, 903—926; compare *Abstr.*, 1891, 285 and 539; 1892, 1068; also 1895, i, 646).—Citronellaldehyde, $\text{CMe}_2\cdot\text{CH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{COH}$ (compare *Abstr.*, 1893, i, 685),

boils at 205—208° under atmospheric pressure, and at 103—105° under a pressure of 25 mm.; the specific rotatory power $[\alpha]_D = +12.5^\circ$, the sp. gr. = 0.8538 at 17.5°, the refractive index $n_D = 1.4481$, and the molecular refraction $M = 48.29$.

Citronellol, $\text{CMe}_2\text{CH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OH}$, was obtained by Dodge on reducing citronellaldehyde with sodium amalgam and glacial acetic acid; it boils at 117—118° under a pressure of 17 mm., has the specific rotatory power $[\alpha]_D = +4^\circ$ at 17.5°, the sp. gr. = 0.8565 at 17.5°, the refractive index $n_D = 1.45659$, and the molecular refraction $M = 49.57$. The *acetate* boils at 119—121° under a pressure of 15 mm., has the specific rotatory power $[\alpha]_D = +2.37^\circ$ at 17.5°, and the sp. gr. = 0.8928 at 17.5°; the refractive index $n_D = 1.4456$ at 17.5°, and the molecular refraction $M = 59.56$. The *formate* boils at 97—100° under a pressure of 10 mm. When citronellol is agitated with 10 per cent. sulphuric acid, a viscous, colourless oil is obtained, boiling at 144—146° under a pressure of 10 mm.; dehydrating agents regenerate citronellol from the substance, which is probably a dihydric alcohol arising from the addition of $1\text{H}_2\text{O}$ to the alcohol.

Oxidation with potassium permanganate, followed by chromic and sulphuric acids, convert citronellaldehyde, citronellol, and citronellic acid into dextro- β -methyladipic acid, which melts at 84—85° (compare Semmler, *loc. cit.*); previous investigators have obtained this substance from menthol, pulegone, menthone, and dimethyl-2 : 6-octanediol-3-oic acid (this vol., i, 247), and the question of its constitution is discussed by the authors.

Isopulegol, $\text{CMe}_2\text{C} < \begin{smallmatrix} \text{CH(OH)}\cdot\text{CH}_2 \\ \text{CH}_2\text{---CH}_2 \end{smallmatrix} > \text{CHMe}$, is obtained in the form of the acetate when citronellaldehyde is heated with an equal weight of acetic anhydride in autoclaves for 10—12 hours at 180—200°, or in presence of anhydrous sodium acetate for 15—20 hours at 150—160°; it has the odour of menthol, boils at 91° under a pressure of 13 mm., and has the specific rotatory power $[\alpha]_D = -2.65^\circ$. The sp. gr. = 0.9154 at 17.5°, the refractive index $n_D = 1.47292$, and the molecular refraction $M = 47.20$.

Isopulegone, $\text{CMe}_2\text{C} < \begin{smallmatrix} \text{CO}\cdot\text{CH}_2 \\ \text{CH}_2\text{---CH}_2 \end{smallmatrix} > \text{CHMe}$, is produced on oxidising isopulegol with acetic and chromic acids, and boils at 85—90° under a pressure of 13 mm., whilst pulegone from polei oil boils at 99—101° under a pressure of 14 mm.; both isomerides are, however, dextrorotatory. When isopulegone is treated with hydroxylamine, pulegoneoxime (m. p. 120—121°), which is volatile in an atmosphere of steam, is produced, as also an *oxime* which melts at 134° and is not volatile. The semicarbazone is identical with the compound from polei oil (Abstr., 1895, i, 380), and when this substance, or the oxime melting at 121° is treated with boiling dilute sulphuric acid and alcohol, it yields methyl-1-cyclohexanone-5 (Wallach, this vol., i, 309).

The authors enumerate several sources of citronellol, and state that the latter may be separated from admixture with geraniol by heating the liquid with phthalic anhydride at 200° for about two hours,

geraniol being converted into the hydrocarbon by this treatment; the phthalic salt of citronellol is then washed and hydrolysed. When the proportion of citronellol in the liquid is small, a method is adopted in which phosphorus trichloride is employed, the alcohols being converted into their phosphates, and then separated.

Turkish rose oil contains 80 per cent. of alcohols, boiling at 112—116° under a pressure of 12 mm.; these consist of geraniol and citronellol in the proportion of three to one. Citronellol obtained from this source has been hitherto called rhodinol, and is lævogyrate, having the rotation $\alpha = -4^{\circ} 20'$ in a 1 decimeter tube; the sp. gr. = 0.8612 at 20°, the refractive index $n_D = 1.45789$, and the molecular refraction $M = 49.43$. Oxidation on the lines indicated for *d*-citronellol converts rhodinol into lævo- β -methyladipic acid, which melts at 84.5°, and has the rotation $\alpha = -2^{\circ}$ in 33 per cent. aqueous solution; when equal weights of *d*- and *l*- β -methyladipic acid are crystallised together, the racemic modification is produced, and crystallises in needles melting at 93—94°. Unlike the odours of bitter almond, vanilla, heliotrope, and violet oils, the perfume of rose oil does not depend on an individual constituent, but is due to several, and the artificial preparation of this scent can no longer be regarded as a purely chemical problem.

Spanish geranium oil contains 70 per cent. of mixed alcohols, consisting of 65 per cent. of geraniol and 35 per cent. of *d*- and *l*-citronellol, of which the latter preponderates; in African geranium oil, the alcohols amount to 75 per cent., of which 80 per cent. is geraniol, whilst 20 per cent. is a lævogyrate mixture of citronellols. Reunion geranium oil (pelargonium oil) contains 80 per cent. of alcohols consisting of 50 per cent. of geraniol.

The recent observation of Barbier and Bouveault, who obtained citronellol and menthone on carefully oxidising pelargonium oil (*Compt. rend.*, 1896, **122**, 737), has not been confirmed by the authors.

M. O. F.

Two Oxygenated Bases from Citronellaldoxime. By FERDINAND TIEMANN and PAUL KRÜGER (*Ber.*, 1896, **29**, 926—928; compare foregoing abstract).—*Amido-4-menthone* (methyl-1-methoethyl-4-amino-4-cyclohexanone-5), $\text{CHMe}_2\text{C}(\text{NH}_2) < \begin{smallmatrix} \text{CO}-\text{CH}_2 \\ \text{CH}_2\cdot\text{CH}_2 \end{smallmatrix} > \text{CHMe}$, obtained from the isomeric citronellaldoxime by dissolving it in 40 per cent. sulphuric acid, boils at 118° under a pressure of 13 mm.; the *acetyl* derivative boils at 142° under a pressure of 12 mm.

Amido-4-menthol, $\text{CHMe}_2\text{C}(\text{NH}_2) < \begin{smallmatrix} \text{CH}(\text{OH})\cdot\text{CH}_2 \\ \text{CH}_2\text{---CH}_2 \end{smallmatrix} > \text{CHMe}$ (methyl-1-methoethyl-4-amino-4-cyclohexanol-5), is formed on reducing the foregoing base with glacial acetic acid and iron, and boils at 125° under a pressure of 12 mm.; it readily absorbs carbonic anhydride from the atmosphere, and the *acetate* crystallises from benzene in slender, white needles, melting at 137°.

The authors regard the production of the former base as analogous to the conversion of camphoroxime into isoamidocamphor.

M. O. F.

Terpenylic acid. By FRIEDRICH MAHLA and FERDINAND TIEMANN (*Ber.*, 1896, **29**, 928—935).—The authors discuss the constitution of terpenylic acid, and, basing their deductions on the accepted formula

for terebic acid, $\begin{array}{c} \text{O-CMe}_2 \\ | \\ \text{CO}\cdot\text{CH}_2 \end{array} > \text{CH}\cdot\text{COOH}$, represent the former substance

by the expression, $\begin{array}{c} \text{O-CMe}_2 \\ | \\ \text{CO}\cdot\text{CH}_2 \end{array} > \text{CH}\cdot\text{CH}_2\cdot\text{COOH}$ (compare Schryver, *Trans.*, 1893, **63**, 1342; also Fittig and Wolff, this vol., i, 135).

The oxidation of terpenylic to terebic acid is described, and also the production of the latter from methoethyl-5-heptanon-2-olide-5¹:7, which may be used profitably as a source of terpenylic acid (compare *Abstr.*, 1894, i, 44). M. O. F.

Campholide, a Product of Reduction of Camphoric Anhydride. By ALBIN HALLER (*Compt. rend.*, 1896, **122**, 293—297).—When an alcoholic solution of camphoric anhydride is reduced by means of sodium amalgam, the liquid being kept acid by addition of sulphuric acid, a small quantity of *campholide*, $\text{C}_{10}\text{H}_{16}\text{O}_2$, is obtained. Aluminium amalgam gives a less satisfactory result.

Campholide forms white crystals, with an odour of camphor, has a hot, burning taste, and is only slightly soluble in water, but extremely soluble in most organic solvents, and its solutions are optically inactive. It melts at 211° (corr.), and sublimes readily. It forms salts with metals, and the copper salt is insoluble in alcohol and water. When oxidised with permanganate, the campholide yields camphoric acid, and when heated with potassium cyanide, it is converted into cyanocampholic acid, from which camphor can be obtained.

This campholide, although similar in composition, differs considerably in properties from the campholide described by M. O. Forster (*Trans.*, 1896, 55). C. H. B.

Convolvulus Resins. By NICOLAI KROMER (*Chem. Centr.*, 1895, ii, 228, 449—450, and 495; from *Zeit. Öster. Apoth. Verein*, 1895, **49**, 418—422, 437—443, 455—459, and 479—484).—Spigatis has shown that scammonin, from *Convolvulus Scammonia* L., is identical with jalapin, from *C. orizabeus* Pell. Purified jalapin is obtained as a colourless, crystalline powder by dissolving the crude product in alcohol (96 per cent.) and allowing the solution to remain during several weeks at a low temperature; it melts at about 142° , the molecular weight = 2000—3000, $[\alpha]_D = -22.84$ to -23.83 , the value for scammonin = -23.06 . The mother liquor contains a compound, $\text{C}_{18}\text{H}_{30}\text{O}$, which crystallises in large, white plates.

By the action of alkali on the glucosides, acids and other substances are formed; lactone derivatives could not be isolated. Both jalapin and scammonin require about 22—23 per cent. of potash for their decomposition.

By the action of baryta water, various substances are formed, of which the portion not volatile with steam and insoluble in ether consists of *jalapic* or *scammonic acid*, $\text{C}_{43}\text{H}_{78}\text{O}_{27}$; it softens at

155—165°, melts at 208°, is feebly acid, and slowly decomposes carbonates; $[\alpha]_D = -29.6^\circ$ to -28.95° . The barium salt has been analysed. The non-volatile product, soluble in ether, possibly consists of a *tetrahydroxydecoic acid*, $C_{10}H_{20}O_6$; the barium and silver salts are crystalline, the latter being deposited in needles; the copper, zinc, and sodium salts have also been prepared. The products of hydrolysis, volatile with steam, consist of methylethylacetic acid and tiglic acid, and, in traces, an acid, probably formic, which reduces silver, gold, and mercury salts.

By the action of dilute acids on the glucosides, a sugar, probably *d*-glucose, and *jalapinic* or *scamminolic acid*, $C_{16}H_{30}O_3$ (?), are produced.

The preceding results show that jalapin and scammonin are identical, but, as the formula of jalapinic acid is doubtful, none can be given for the glucoside. Turpethin, the active constituent of the root of *Ipomœa turpethum* (Abstr., 1893, i, 424), is identical with jalapin in percentage composition; when treated with baryta water, *turpethic acid* is formed, which is colourless and not volatile with steam. The behaviour of jalapic acid towards litmus and phenolphthaleïn suggests that it may be a phenol. J. B. T.

Acokanthera Schimperii. By THOMAS R. FRASER and JOSEPH TILLIE (*Pharm. J. Trans.*, 1895, 55, 76).—The authors have been able to refer several specimens of wood, from which native tribes in East Africa prepare arrow poison, to the genus *Acokanthera*. They have extracted from the leaves, flowers, and fruit of *Acokanthera schimperii* the active principle as a crystalline glucoside, $C_{30}H_{48}O_{13}$, identical with that contained in the wood. It is very soluble in water, from which it crystallises in colourless, transparent, quadrangular plates. From alcohol, in which it is much less soluble, it separates in needle-shaped crystals. The aqueous solution is neutral in reaction and tasteless. Few chemical reagents affect it, but strong sulphuric acid produces at once a red colour, and this afterwards changes to green. With dilute sulphuric acid, it gives the reaction of a glucoside. The characters of this active principle agree with those of the glucosides that have been separated from the woods of several unidentified species of *Acokanthera*, and with that derived from a species of *Strophanthus* obtained from West Africa. R. R.

Ricinin. By MARCO SOAVE (*Chem. Centr.*, 1895, i, 853; from *Ann. Chim. Farm.*, 21, 49—61).—*Ricinin*, $C_{17}H_{15}N_4O_4$, is the poisonous principle of the castor oil seeds. The pressed seeds yield 0.3 per cent., whereas the husks yield 1.5 per cent. of ricinin. To obtain the ricinin, the pressed seeds or husks are extracted with boiling water, the extract evaporated on the water bath, and the residue treated with alcohol. The alcoholic solution is then evaporated to dryness and the residue treated with caustic soda; by this means, the impurities are dissolved out, and the ricinin which remains behind may be crystallised from alcohol or water. It crystallises in glistening plates, melts at 194°, has a bitter taste, is readily soluble in water, alcohol, chloroform, benzene, and

ether; the aqueous solution is neutral and optically inactive. Ricinin may be sublimed when carefully heated; it is soluble in concentrated sulphuric acid, yielding a colourless solution, which becomes straw-yellow, and then bright claret red, on warming. The colourless sulphuric acid solution gives, with a crystal of potassium dichromate, a bright green coloration; the author suggests this as a test for ricinin. Ricinin does not give the usual tests for alkaloids, neither does it form salts with strong mineral acids; it yields a bromo-derivative, $C_{17}H_{16}Br_2N_4O_4$, which melts at 247° , and a corresponding chloro-derivative, which melts at 240° . With mercuric chloride, it yields the compound, $C_{17}H_{13}N_4O_4 \cdot 2HgCl_2$, which melts at 204° . When oxidised, it yields a new acid, $C_{15}H_{14}N_4O_4$, which the author terms *ricininic acid*; the same acid may also be obtained by the hydrolysis of ricinin with caustic soda. It is a dibasic acid, which melts at 295° , yields a silver salt, a barium salt crystallising with $4H_2O$, and a bromo-derivative, $C_{15}H_{12}Br_2N_4O_4$, melting at 180° . J. J. S.

Polystichic acids. By C. POULSSON (*Chem. Centr.*, 1895, i, 887; from *Arch. Exp. Path. Pharm.*, 1894, **35**, 97—104).—The author has obtained two new acids from the rhizomes of *Polystichum spinulosum*, taken in the autumn. One of these is *polystichic acid*, $C_{22}H_{24}O_9$, which melts at 123 — 123.2° ; it is insoluble in water, readily soluble in chloroform, ether, and benzene, and crystallises in yellowish needles. The second acid is *dihydropolystichic acid*, $C_{22}H_{26}O_9$, which crystallises in white, granular masses or colourless needles, and melts at 150° . The two acids are best separated by crystallisation from acetone and then by treatment with chloroform and methylic alcohol. Both are poisonous, and resemble flicic acid in their physiological action. The fatal dose for frogs is 2 milligrams, for rabbits 0.03—0.05 gram per kilo. of body weight. J. J. S.

Turmerole. By C. LORING JACKSON and WILLIAM H. WARREN (*Amer. Chem. J.*, 1896, **18**, 111—117).—Turmerole, a compound obtained from the oily extract of turmeric (*Abstr.*, 1883, 482), was purified by fractional distillation under reduced pressure. It is a yellowish oil, with a peculiar, agreeable odour, and its sp. gr. = 0.9561 at $24^\circ/4^\circ$. It mixes easily with the common solvents, but is insoluble in water. It is partially decomposed by distillation under the ordinary pressure, but distils unchanged between 158° and 163° at 11—12 mm. pressure. Analyses of different fractions agreed in indicating the formula $C_{13}H_{18}O$, or possibly $C_{14}H_{20}O$. Dilute nitric acid converted turmerole into paratoluic acid. Turmerole therefore contains a benzene ring with a methyl group, and a side-chain of six or seven carbon atoms in the positions 1:4. The side-chain contains an asymmetric carbon atom, the specific rotation of turmerole being $[\alpha]_D = 24.58^\circ$. A. E.

Chemistry of Red Vegetable Colouring Matters. By LEOPOLD WEIGENT (*Bied. Centr.*, 1896, **25**, 58—59; from *Jahresber. k. k. Wein u. Obstbaulehranst. Klosterneuburg*, 1894—95).—There are two groups of red dyes (1) wine-red, including the colouring matter of grapes, reddened vine leaves, leaves of the wild vine, *Rhus typhina*, *Cornus sanguinea*,

&c. They give the following reactions: lead acetate, bluish-green or grey precipitates; cold concentrated hydrochloric acid, brighter red coloration and precipitation; ammonia, alkalis or alkaline earths, greenish colour. Group (2) includes the red dyes of beet-root, the leaves of iresine, amaranth, and achyranthes, and the fruit of *Phytolacca decandra*. With lead acetate, these dyes yield red precipitates, but do not give Erdmann's reaction, and are changed to dark violet by strong, cold hydrochloric acid. In slightly alkaline solutions, they retain their red colour, but excess of ammonia gives a dark violet, and excess of alkalis and alkaline earths first violet-brown, then a bright yellow coloration. The red dye is not extracted from the dried plants by alcohol, but dissolves in water.

Wine-red is nearly related to the violet or dark red dyes of *Coleus Verschaffelti*, *Perilla nankinensis*, *Ajuga reptans*, *Prunus Pissardi*, and the bluish-skinned potato cabbage, the blue bean, and the mallow.

Blue grapes and bilberries contain a red-brown dye, insoluble in acidified water, and a soluble dye, which, when boiled with acid, yields sugar and the insoluble dye. The deposition of the colouring matter of red wine is due to the conversion of the soluble into the insoluble dye. There seems to be no direct connection between these dyes and chlorophyll, but they protect chlorophyll from the action of light. Red autumn leaves show much less evaporation than green leaves.

N. H. J. M.

Mercurypyridine Compounds. By LEONE PESCI (*Gazzetta*, 1895, 25, ii, 423—433; compare this vol., i, 186).—*Pyridine mercurio-* (*mercurypyridine*) *chloride*, $(C_5NH_5)_2HgCl_2$, formed with development of heat on treating mercuric chloride with pyridine, crystallises from pyridine in colourless, lustrous needles melting at 108° . It is decomposed on boiling with alcohol or water, yielding Lang's salt, $(C_5NH_5)_2HgCl_2 \cdot HgCl_2$ (*Ber.*, 1888, 1586), which crystallises in colourless needles melting at 120 — 180° . Monari's salt,



crystallises in lustrous, colourless needles melting at 194 — 195° . *Pyridine mercuric hydroxide*, $(C_5NH_5)_2Hg(OH)_2$, can only be obtained in aqueous solution by treating the corresponding chloride with silver hydroxide or by the prolonged boiling of yellow mercuric oxide with aqueous pyridine solution. It is most conveniently prepared by adding excess of barium carbonate to pyridine mercuric sulphate solution; the filtrate from the carbonate and sulphate deposits basic mercuric carbonate, $3HgO \cdot CO_2$, in lustrous red needles. The solution of the hydroxide is colourless and strongly alkaline, and has the odour and taste of aqueous pyridine solution; it deposits yellow mercuric oxide on evaporation, and, when evaporated with nitric acid, deposits *pyridine mercuric nitrate*, $(C_5NH_5)_2Hg(NO_3)_2 \cdot 2H_2O$, which crystallises in colourless needles, and effloresces in a dry atmosphere. The corresponding *sulphate*, $(C_5NH_5)_2HgSO_4 \cdot 4H_2O$, is prepared by adding mercuric sulphate and a little yellow mercuric oxide to pyridine solution; it crystallises in large, monoclinic prisms which are very soluble in water, and lose $2H_2O$ in dry air.

W. J. P.

2 : 6-Diphenylpyridine and Piperidine. By CARL PAAL (*Ber.*, 1896, **29**, 798—800).—2 : 6-Diphenylpyridine was prepared by Scholtz from cinnamylideneacetophenone oxime (*Abstr.*, 1895, i, 562), by Paal and Strasser from diphenacylmalonic acid, and by Doebner and Kuntze from α -phenylnaphthocinchonic acid; although the bases are identical, the platinochlorides described by Scholtz and by Paal differ in melting point and solubility; they have, therefore, been reinvestigated, and are found to be identical, the differences being due to impurity in Paal and Strasser's preparation. The compound melts at 195°, and is sparingly soluble. 2 : 6-Diphenylpiperidine was previously described as an oil both by Paal and Strasser, and by Scholtz. If prepared from purified diphenylpyridine, it crystallises from alcohol, on the addition of water, in large, colourless, transparent plates melting at 69°. The hydrochloride melts at 298°, but, after treating it with ether, regenerating the base, and reconverting it into the hydrochloride, the latter melts at 315—316°. The impurity in the diphenylpiperidine appears to have been derived from the common quicklime employed for the decomposition of the diphenyldipiperidinedicarboxylic acid.
J. B. T.

Reactions of Ethylic Orthonitrobenzylmalonate. I. Alkaline Hydrolysis; Synthesis of new Indole Derivatives. By ARNOLD REISSERT (*Ber.*, 1896, **29**, 639—665; compare this vol., i, 392).—When ethylic orthonitrobenzylmalonate is heated with 33 per cent. aqueous soda, the normal reaction occurs, and *orthonitrobenzylmalonic acid*, $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{C}(\text{COOH})_2$, is formed; it crystallises in colourless, rectangular prisms, which melt and evolve gas at 161°. The *hydrogen ammonium salt*, obtained by adding hydrochloric acid to the normal salt, crystallises in prisms melting at 169°; the *normal salt* is more readily soluble in water, and melts at 172°. The *silver salt* is an amorphous, white precipitate.

When ethylic orthonitrobenzylmalonate is heated with an excess of alkali or boiled with alkali for some time, or when orthonitrobenzylmalonic acid is boiled with aqueous soda, *1'-hydroxyindole-2'-carboxylic acid* is formed; it crystallises in stellate groups of small, white prisms which melt at 159.5°. The acid reduces Fehling's solution when heated, gives a cherry-red coloration with nitric acid, and dissolves in sulphuric acid, forming a colourless solution which becomes blue on heating. The alkaline solutions of the acid gradually become indigo coloured when kept; with bleaching powder, the aqueous solution of the acid gives a blue precipitate resembling indigo, whilst chromic acid produces a red precipitate. The salts are unstable, and not characteristic. The *methyl salt*, $\text{C}_6\text{H}_4\text{NO}\cdot\text{COOMe}$, crystallises in long, snow-white, lustrous needles, and melts at 100—101°. The *ethylic salt* crystallises in colourless, pointed prisms melting at 65°.

The *1'-benzoyl-derivative*, $\text{C}_6\text{H}_4\langle\text{N}(\text{OBz})\rangle\text{C}\cdot\text{COOH}$, forms snow-white, small crystals melting and decomposing at 151°. Acetic anhydride in the cold produces two compounds. The *mixed anhydride*

of acetic and hydroxyindolecarboxylic acids, $C_{13}H_{11}NO_5$, forms colourless, lustrous needles which melt at 107° , and is decomposed by boiling water. 1'-Acetoxyindole-2'-carboxylic acid forms small, white needles, and melts at 161° . It dissolves without change in sodium hydrogen carbonate solution, but is at once hydrolysed by aqueous soda. 1'-Methoxyindole-2'-carboxylic acid is obtained by the action of sodium ethoxide and methylic iodide on the acid; it crystallises in lustrous, well-developed needles, and melts and decomposes at 185° . This acid is very stable, and is not acted on by Fehling's solution, ferric chloride, sodium nitrite, or hydrogen peroxide. The silver salt is soluble in a large amount of hot water. Methylic 1'-methoxyindole-2'-carboxylate is obtained by the action of methylic alcohol and hydrogen chloride on the acid just described, and by the action of sodium methoxide and methylic iodide on methylic hydroxyindolecarboxylate. It forms short, thick, rhomboid crystals, and melts at 68° . 1'-Methoxyindole-2'-carboxylic chloride crystallises in long, white needles melting at 61° . The amide crystallises in plates which resemble those of benzoic acid, and melt at 108° . Bromine converts the amide into a derivative which melts at 175° . 3':1'-Bromomethoxyindole-2'-carboxylic acid, $C_{10}H_9NO_3Br$, crystallises in short, lustrous needles, and melts at 189° . Hydroxyindolecarboxylic acid is converted by reduction by means of zinc dust and acetic acid into the well-known α -indolecarboxylic acid melting at about 203° . The same acid is formed when the methoxy-acid is reduced with sodium amalgam.

Potassium permanganate converts hydroxyindolecarboxylic acid into the orthazoxybenzoic acid which was first described by Griess *Ber.*, 1874, 7, 1611). Chromic acid, on the other hand, converts the acid into isatin. The methoxy-acid is converted by this reagent into 1'-methoxypseudoisatin, $C_8H_4\langle\overset{CO}{\text{N(OMe)}}\rangle CO$, which forms small, brick-red needles, and melts at 110° . It resembles isatin in appearance, and gives, with sulphuric acid and thiophen, a reaction which closely resembles the indophenine reaction. It reduces Fehling's solution when warmed, and dissolves in alkalis. The phenylhydrazone melts at 128 — 129° . When reduced, methoxypseudoisatin appears to be converted into dioxindole. Indoxin, $C_{18}H_{12}N_2O_4$, is formed when hydroxyindolecarboxylic acid is treated with hydrogen peroxide, or when the mixed anhydride of acetic and hydroxyindolecarboxylic acids is treated with aqueous soda. It is a blue, crystalline substance which melts at 223° , and resembles indigo-blue very closely in appearance. It is soluble in hot water, the solution being decolorised by the addition of hydrochloric acid; it also dissolves in solutions of caustic alkalis, but not of their carbonates.

Nitrous acid converts the hydroxyindolecarboxylic acid into a nitramine, 1'-nitroindole-2'-carboxylic acid, $C_8H_4\langle\overset{CH}{\text{N(NO)}_2}\rangle C\cdot COOH$, which forms a lemon-yellow, micro-crystalline deposit, and melts and decomposes at 189° . It does not give Liebermann's reaction, neither does it form a benzoyl derivative. When methylic hydroxyindolecarboxylate is treated with nitrous acid, it forms an unstable, crystal-

line substance melting at $224-225^{\circ}$, the constitution of which has not been determined; if this is dissolved in dilute alkali and the solution acidified, the nitramine described above is precipitated. The substance melting at $224-225^{\circ}$ is converted by boiling with ammonium sulphide into a crystalline base, which melts at 136° , and is probably *methylic 1'-amidoindole-2'-carboxylate*. The compound melting at $224-225^{\circ}$ is accompanied by another substance which appears to have the composition $C_{10}H_9NO_3$, but has not yet been obtained pure.

A. H.

Improvement of Skraup's Quinoline Synthesis. By CHR. A. KNUEPPEL (*Ber.*, 1896, **29**, 703—709).—As is well known, the usual method of preparing a quinoline derivative is to heat the corresponding aromatic amido-derivative with glycerol in the presence of strong sulphuric acid and nitrobenzene. The last substance acts as an oxidising agent, but a much better yield is obtained if it is replaced by arsenic acid; only in the case of quinoline itself, in which case the nitrobenzene also takes part in the synthesis, was a larger yield obtained by the old method. To take an example, β -naphthaquinoline was prepared by heating together 100 grams of arsenic acid, 200 grams of concentrated sulphuric acid, 215 grams of glycerol, and 100 grams of commercial β -naphthylamine in the oil bath until the action began; when this had moderated, the flask was replaced in the bath, and the contents gently boiled for 3—4 hours. The mixture was then diluted with water, allowed to settle for some time, filtered, and the filtrate made alkaline with sodium hydroxide, when the naphthaquinoline separated as an oil that soon solidified. It was purified by boiling it in alcoholic solution with animal charcoal, and adding water to the filtered solution; the yield was 92—93 grams, melting at 93.5° . In a similar way there were prepared quinoline itself, and 1-methylquinoline, 1-nitroquinoline, 3-nitroquinoline, 3-dimethylamidoquinoline, 2-nitroquinoline, 2-dimethylamidoquinoline, β -anthraquinoline, dihydroxy- β -anthraquinoline (alizarin blue), and quinoline-3-sulphonic acid.

C. F. B.

1 : 4-, 1 : 3-, and 2 : 4-Dinitroquinoline. By ADOLPH CLAUS and GABRIEL HARTMANN (*J. pr. Chem.*, 1896, [2], **53**, 198—210).—1 : 4-Dinitroquinoline has been previously described as α -dinitroquinoline (*Abstr.*, 1885, 908); conversion into 1 : 4-dibromoquinoline through the diazo-reaction has settled its orientation. The *hydrobromide* forms yellow crystals, melts at 230° , and readily combines with bromine to form a dibromide, which is convertible, in the usual manner (Claus-Collischon's method), into a 3'-bromo-1 : 4-dinitroquinoline. This crystallises in colourless needles, and melts at 152° .

4 : 1-Nitramidoquinoline was prepared by reducing the dinitroquinoline with ammonium sulphide; it forms columnar crystals, melts at 184° , and is a feeble base; replacement of the amido-group by a bromine atom gave a bromonitroquinoline, which has been already orientated; the *methiodide* is described; the *platinochloride* melts and decomposes at 246° . 4 : 1-Nitracetamidoquinoline sublimes in the

form of transparent, yellow needles, melts at 220° , and is sparingly soluble in hot water and hot alcohol.

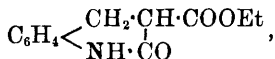
1 : 3-Dinitroquinoline (β -dinitroquinoline, *loc. cit.*) melts at 144° , not 133 — 134° (*loc. cit.*); by bromination it yields a 3'-bromo-1 : 3-dinitroquinoline, which crystallises in colourless needles, melts at 120° , and dissolves in alcohol sparingly, and in water not at all.

3 : 1-Nitramidoquinoline crystallises in lustrous, red needles or columns, melts at 194° , and is sparingly soluble in hot water, but more freely in hot alcohol; the methiodide crystallises in red, lustrous needles, melts at 176° , and dissolves easily in hot alcohol, but only sparingly in cold water; the platinochloride is described. The easy formation of a methiodide seems to characterise amido-compounds in which the amido-group is in the 1-position. 3 : 1-Nitracetamidoquinoline sublims in lustrous, yellow needles, melts at 224° , and is not very soluble either in water or alcohol.

2 : 4-Dinitroquinoline sublims in the form of yellow, lustrous needles, melts at 179° , and is freely soluble in alcohol, ether, and chloroform, but not in water; the hydrochloride forms colourless crystals, and melts at about 86° ; the platinochloride was prepared. By bromination, the dinitroquinoline yields a 3'-bromo-2 : 4-dinitroquinoline, which crystallises in colourless needles, melts at 161° , and sublims unchanged.

A. G. B.

Reactions of Ethylic Orthonitrobenzylmalonate. II. Reduction : Formation of Quinoline Derivatives. By ARNOLD REISSERT (*Ber.*, 1896, 29, 665—667).—When ethylic orthonitrobenzylmalonate is dissolved in alcoholic hydrogen chloride and treated with zinc dust, it is converted into ethylic hydrocarbostyryl-3'-carboxylate,



which crystallises in matted needles, melting at 137 — 138° . The free acid crystallises in short, thick prisms, and melts with evolution of carbonic anhydride at 146° , being thereby converted into hydrocarbostyryl. The acid is readily soluble in acetic acid, alcohol, and hot water. The silver salt is soluble in hot water.

A. H.

New Bromo-derivatives of Carbazole. By GIROLAMO MAZZARA and ARISTIDE LEONARDI (*Gazzetta*, 1895, 25, ii, 395—400; compare this vol., i, 304).—An improved method of preparing benzoyldibromocarbazole is described. No products of interest are obtained by the action of nitric acid on dibromocarbazole; its benzoyl derivative, however, when heated with nitric acid (sp. gr. 1.46) yields the bromodinitrocarbazole, melting at 255° .

Diamidocarbazole is formed on reducing dinitrocarbazole with tin and hydrochloric acid, but no nitramidocarbazole could be obtained. On nitrating the nitramidocarbazole melting at 213 — 214° in acetic acid solution, a nitracetamidocarbazole, which crystallises in minute yellow needles, is obtained, and, on hydrolysis with potash, yields a nitramidocarbazole; the latter is a crystalline, red powder, which

does not melt, and of which the amidogen cannot be replaced by bromine.

Acetyldibromocarbazole is obtained from dibromocarbazole in the usual way, and crystallises in white needles, melting at $189-190^{\circ}$ (corr.); on nitration, it yields bromine, polynitro-derivatives, and the bromodinitrocarbazole melting at 255° .

Benzoyltribromocarbazole is obtained, together with the dibromocompound, on heating a carbon bisulphide solution of benzoylcarbazole with bromine; it crystallises in transparent, yellow laminae or needles, melting at $228-230^{\circ}$, and is not attacked by boiling alcoholic potash.

Pentabromocarbazole, $C_{12}H_4NBr_5$, is prepared by boiling a chloroform solution of carbazole with bromine and a little iodine; it crystallises in minute, white needles melting at $273-274^{\circ}$, and is not acted on by acetic anhydride at 240° .

Heptabromocarbazole may be prepared by heating dibromocarbazole with bromine at 100° in a closed tube; it crystallises in whitish needles, which do not melt at 330° . W. J. P.

Cyanalkines; Cyanobenzylidine [4-Amido-5-phenyl-2 : 6-dibenzylmetadiazine]. By G. HERFELDT (*J. pr. Chem.*, 1896, [2], 53, 246-250; compare Abstr., 1889, 684).—Cyanobenzylidine (4-amido-5-phenyl-2 : 6-dibenzylmetadiazine) is best prepared by mixing dry sodium ethoxide with benzylic cyanide to a stiff paste, and heating the mixture in an autoclave for 6-8 hours at $160-170^{\circ}$; the product is treated with water, and crystallised from alcohol. *Bromocyanobenzylidine*, $C_{24}H_{20}BrN_3$, the sole substitution product obtained by brominating cyanobenzylidine, forms small, white crystals, and is converted into *bromo-4-hydroxy-5-phenyl-2 : 6-dibenzylmetadiazine*, $C_{24}H_{18}BrN_2OH$, when heated with strong hydrochloric acid at 140° ; this melts at 120° .

Chlorocyanobenzylidine forms pale yellow crystals, and melts at 65° . The *methiodide*, $C_{24}H_{21}N_3MeI$, was prepared, and from it the *platinichloride*, $(C_{24}H_{20}MeN_3)_2, H_2PtCl_6$, but the corresponding base was not isolated. The action of methylic iodide on the hydroxy-derivative (m. p. 180° , *loc. cit.*) yielded the *methyl* derivative, $C_{24}H_{18}MeN_2OH$, which crystallises in white needles, and melts at 135° .

Cyanobenzylidine (1 mol.) combines with acetic chloride (1 mol.) to form an additive compound, which melts at 116° , the corresponding benzoic chloride derivative melting at 129° . The cyanethine acetic chloride melts at 142° ; cyanopropine acetic chloride at 210° . The additive compound of phenylcarbimide and cyanobenzylidine melts at 162° .

The action of nitrous acid on cyanobenzylidine does not produce a compound analogous to that obtained by such treatment of cyanethine (Abstr., 1889, 685), but a compound, $C_{24}H_{15}N_3O_5 \cdot \frac{1}{2}H_2O$, which crystallises in yellow, felted needles, and melts at 210° . A. G. B.

Methyldioxytriazine (Acetoguanamide). By ADRIANO OSTROGOVICH (*Gazzetta*, 1895, 25, ii, 442-446).—On heating acetylurethane and carbamide in a closed tube at $148-150^{\circ}$ for six hours, VOL. LXX. i. 2 f

and crystallising the product from water, acetoguanamide is formed in accordance with the equation $\text{COMe}\cdot\text{NH}\cdot\text{COOEt} + \text{CO}(\text{NH}_2)_2 = \text{CO} < \begin{smallmatrix} \text{NH}\cdot\text{CMe} \\ \text{NH}\cdot\text{CO} \end{smallmatrix} > \text{N} + \text{H}_2\text{O} + \text{EtOH}$.

Argentoacetoguanamide, $\text{C}_4\text{H}_4\text{N}_3\text{O}_2\text{Ag}$, is a white flocculent powder.
W. J. P.

Dichloroquinoxaline Derivatives. By OSCAR HINSBERG and J. POLLAK (*Ber.*, 1896, **29**, 784—787).—Dihydroxyquinoxaline, prepared from orthophenylenediamine and oxalic acid, is converted into 2':3'-dichloroquinoxaline, $\text{C}_6\text{H}_4 < \begin{smallmatrix} \text{N}:\text{CCl} \\ \text{N}:\text{CCl} \end{smallmatrix} > \text{C}_6\text{H}_4$, by heating with phosphorus pentachloride at 160° ; it is deposited from alcohol in colourless crystals, and melts at 150° .

Fluoflavine, $\text{C}_6\text{H}_4 < \begin{smallmatrix} \text{N}:\text{C}\cdot\text{NH} \\ \text{N}:\text{C}\cdot\text{NH} \end{smallmatrix} > \text{C}_6\text{H}_4$, is prepared by heating dichloroquinoxaline (1 mol.), orthophenylenediamine (2 mols.), and anhydrous sodium chloride at 120 — 130° , or by heating dihydroxyquinoxaline, or oxalic acid with orthophenylenediamine at 240° ; the yield is about 50 per cent. of the theoretical, and less than that obtained by the first method. The compound crystallises from glacial acetic acid in deep yellow needles and melts at 360° . Its acetic acid solution is dark yellow with a yellowish-green fluorescence, sulphuric acid gives a yellow solution; in other media, it is insoluble. When boiled with soda and alcohol, it slowly dissolves giving a green liquid; it is stable towards reducing agents and acetic anhydride. The *hydrochloride*, $\text{C}_{14}\text{H}_{10}\text{N}_4\cdot 2\text{HCl}$, is yellow, and decomposes in presence of water.

Quinoxalophenazine, $\text{C}_6\text{H}_4 < \begin{smallmatrix} \text{N}:\text{C}\cdot\text{N} \\ \text{N}:\text{C}\cdot\text{N} \end{smallmatrix} > \text{C}_6\text{H}_4$, or $\text{C}_6\text{H}_4 < \begin{smallmatrix} \text{N}:\text{C}\cdot\text{N} \\ \text{N}:\text{C}\cdot\text{N} \end{smallmatrix} > \text{C}_6\text{H}_4$, is prepared by the oxidation of fluoflavine, preferably by means of glacial acetic acid and potassium dichromate; it crystallises from chloroform in reddish-brown plates or needles melting above 370° . When boiled with alcoholic soda, it gives a blue solution; it dissolves also in sulphuric acid with a brownish-yellow coloration, and on dilution the colour changes to brownish-red, and the *sulphate* is deposited; when heated with quinol, fluoflavine is regenerated and quinone is produced. When treated with concentrated hydrochloric acid, it is converted into *chlorofluoflavine*, $\text{C}_6\text{H}_4 < \begin{smallmatrix} \text{N}:\text{C}\cdot\text{NH} \\ \text{N}:\text{C}\cdot\text{NH} \end{smallmatrix} > \text{C}_6\text{H}_3\text{Cl}$, which is deposited from glacial acetic acid in yellow crystals, melts above 360° , closely resembles fluoflavine in general properties, and when oxidised yields a *chlorazine*; the stability of the chlorine atom indicates that it is present in one of the benzene rings.

Phenylfluoflavylsulphone, $\text{C}_6\text{H}_4 < \begin{smallmatrix} \text{N}:\text{C}\cdot\text{NH} \\ \text{N}:\text{C}\cdot\text{NH} \end{smallmatrix} > \text{C}_6\text{H}_3\cdot\text{SO}_2\text{Ph}$, prepared by the interaction of quinoxalophenazine and phenylsulphinic acid, in presence of glacial acetic acid, is a deep yellow, crystalline powder melting above 340° , its colour and fluorescence are stronger than

those of fluoflavine; with alcoholic soda, it gives a yellowish-green solution, and when oxidised, it yields the corresponding phenazine.

J. B. T.

Reduction Products of Cinchona Alkaloids. By FRITZ KONEK VON NORWALL (*Ber.*, 1896, **29**, 801—805).—The reduction of cinchonidine, quinine, and quinidine, is effected in the same manner as that of cinchonine (*Abstr.*, 1895, i, 631), the resulting tetrahydro-bases are oily and readily yield nitroso-nitrites with the general formula, $C_5H_4 \cdot \begin{matrix} CH(X:N, HNO_2) \\ \diagup \quad \diagdown \\ N(NO) \cdot CH_2 \cdot CH_2 \end{matrix} [X = C_{10}H_{15}O]$. These are converted by alkali into nitroso-bases which give Liebermann's reaction, but no coloration with chlorine, or bromine water. By the action of zinc and acid, resinuous products are formed. The yield of nitrosomitrite from cinchonine is quantitative and from quinine very good, but from the others it is poor; this corresponds with the behaviour of the alkaloids when oxidised.

Tetrahydrocinchonidine nitrosomitrite crystallises in yellow, lustrous needles melting and decomposing at 192—193°, but when rapidly heated the melting point is a few degrees higher; it is less soluble than the cinchonine derivative, and differs from it both in colour and in crystalline form. The *nitroso-base* is a yellow oil; the *methiodide* is pale yellow; the *hydrochloride* and *oxalate* are crystalline.

Tetrahydroquinine nitrosomitrite is at first the colour of peach blossom but quickly darkens and finally becomes pale yellow; it crystallises in glistening, yellow needles, melting and decomposing at 188°; when boiled for a few moments, nitrous anhydride is evolved and the liquid becomes olive green and gives, with ammonia, a red, flocculent precipitate. The *nitroso-base* is rose coloured.

Tetrahydroquinidine nitrosomitrite crystallises from water in deep yellow, lustrous needles, and from dilute alcohol in yellowish-brown prisms, melting at 178—179°. The *nitroso-base* is white and gives a blue coloration with phenol and sulphuric acid.

J. B. T.

Action of Heat on the Alkaloids of Ipecacuanha. By BENJAMIN H. PAUL and ALFRED J. COWNLEY (*Pharm. J. Trans.*, 1895, [4], **1**, 2).—Solutions of emetine and of cephaeline in excess of acetic acid can be boiled for a long time without change, but if they are evaporated in an open basin and the dry residue heated on a water bath for 16 hours, considerable darkening occurs, and there is a loss of alkaloid, amounting to 27 per cent. in the case of emetine, and 22 per cent. in the case of cephaeline. The presence of air appears necessary for the alteration.

R. R.

Ipecacuanha. By RICHARD A. CRIPPS (*Pharm. J. Trans.*, 1895, [4], **1**, 159—161).—Ipecacuanha was treated with ether and the residue extracted with rectified spirit. The alcoholic extract was evaporated, the residue extracted with chloroform while still acid, then made alkaline with ammonia and extracted with ether. The alkaloid obtained in this way was dissolved in alcohol, an equal volume of ether added, and then more ether containing about 0.25 per cent. of hydrogen chloride, whereby a white precipitate was formed; the clear liquid was

poured off, and more ethereal hydrogen chloride added in successive portions, until the whole of the alkaloid had been precipitated in several fractions.

The 1st and 5th of these were taken for conversion into the aurochloride and platinochloride. The aurochlorides were found to be practically identical, and agreed with Paul's formula for emetine. Neither of the platinochlorides corresponded with that of cephaeline. It is concluded that the alkaloid soluble in ether in this sample of ipecacuanha consisted solely of emetine. No trace of Arndt's volatile alkaloid was detected.

R. R.

Chelidonium Alkaloids. By N. A. ORLOFF (*Chem. Centr.*, 1895, ii, 226 and 305; from *Pharm. Zeit. Russ.*, **34**, 369—371 and 385—390).—Chelerythrine is contained in all parts of fresh specimens of *Chelidonium majus*, but none could be extracted from the dried plants. The fruit contains 0.06 per cent., and the root 0.001—0.005 per cent. of the alkaloid. The plant is extracted with water containing a little sulphuric acid, the extract treated with potassium carbonate, and the washed and dried precipitate extracted with ether; the alkaloid is then converted into the yellow, oily *sulphate*, and this is decomposed by means of ammonia. The *hydrochloride* is orange-yellow, but the base is colourless. *Chelilysine* is present both in the fresh and dried plants; these are extracted with water, the solution treated with soda, and the filtrate precipitated with tannin; the dried precipitate is then extracted with alcohol, the solution acidified with hydrochloric acid, and the hydrochloride further purified. It gives precipitates with platinic chloride, auric chloride, phosphotungstic acid, phosphomolybdic acid, and potassio-bismuth iodide. The yield of hydrochloride is 0.007 per cent. The base is amorphous and almost insoluble in chloroform and ether.

J. B. T.

Scopoleïne. By WALTER LUBOLDT (*Chem. Centr.*, 1895, i, 546; from *Apoth. Zeit.*, 1894, **9**, 931—932; compare *Abstr.*, 1895, i, 632).—*Tropylscopoleïne* is best prepared according to Liebermann and Limpach's method, by heating tropic anhydride with scopoline at 230°; the base may be extracted from the resulting brown mass by means of very dilute hydrochloric acid. It is also formed when scopoline is melted with tropide, or by the prolonged heating of natural scopolamine at 230°. The free base is a soft, amorphous substance, which melts at 166°; it is practically insoluble in water, readily soluble in chloroform and dilute acids, and only moderately in alcohol and ether. Neither the base itself nor its salts could be obtained in a crystalline form.

The *hydrobromide* is precipitated by ether from its alcoholic solution as a white, amorphous powder, which is extremely deliquescent. The *hydrochloride* is a yellowish, deliquescent, amorphous powder, which is readily soluble in water and alcohol. The *sulphate* and *nitrate* are sparingly soluble in alcohol; the *aurochloride* is a yellow, amorphous powder, sparingly soluble in boiling water, and melts at 180°; the *platinochloride* melts at 246—248°.

Analyses point to the composition $C_{17}H_{21}NO_4$ for the base, and it is therefore isomeric with the natural scopolamine. J. J. S.

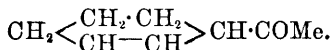
Alkaloids from the Rind of Pomegranate Root. By GIACOMO L. CIAMICIAN and PAUL SILBER (*Ber.*, 1896, **29**, 481—489; compare *Abstr.*, 1892, 1110; 1893, i, 287; 1894, i, 154; 1895, i, 160).—The alkaloids of the pomegranate root appear to be derived from a substance in which the carbon and nitrogen atoms are arranged as follows,

$$C \begin{array}{c} \swarrow N \cdot C \cdot C \searrow \\ \leftarrow C \rightarrow \\ \swarrow C \cdot C \cdot C \searrow \end{array} C.$$
 The authors propose to name the fundamental

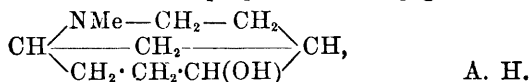
substances obtained in the course of their investigations as follows. Granatanine, C_8NH_{15} ; granateniue, C_8NH_{13} ; granatoniué, $C_8NH_{11}O$; granatoline, $C_8NH_{11} \cdot OH$.

Oxygranatanine, $C_8NH_{15}O$, is formed by the action of alkaline permanganate on granatanine. The *hydrochloride* crystallises in slender, white needles, and melts and decomposes at 225° . The *platinochloride* decomposes at 230° . The *benzoyl derivative* melts at $69-70^\circ$.

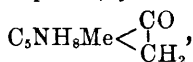
When granatal (dihydrogranatone) is oxidised by means of alkaline permanganate, it is converted into normal adipic acid, which is identical with the acid prepared by other methods. The pure acid melts at $153-153.5^\circ$ (corr.), and has the following crystallographic constants, which have not previously been determined; $a:b:c = 1.9637:1:1.79$; $\beta = 42^\circ 55'$. Tropilene, the corresponding derivative in the tropine series, yields the same acid on oxidation. Granatal, therefore, appears to be tetrahydroacetophenone,



When methylgranatoline is submitted to oxidation, it is converted into *granatic (homotropinic) acid*, $C_9H_{13}NO_4$, which crystallises in small, colourless prisms, and melts and decomposes at $240-245^\circ$. The *aurochloride* melts and decomposes at 190° . This acid is very similar to tropinic acid, and is probably methylpiperidinecarboxyacetic acid. This would agree well with the formula proposed for methylgranatoline,



n-Methyltropone. By GIACOMO L. CIAMICIAN and PAUL SILBER (*Ber.*, 1896, **29**, 490—493).—Methylgranatoline is converted by oxidation into methylgranatonine, the corresponding ketone. In the same way tropine (methyltropoline) yields *methyltropone*,



which crystallises in long, broad, colourless needles, melting at 42° , and is deliquescent. The *aurochloride* melts at 163° with decomposition. *n-Methyltroponeoxime* crystallises in colourless prisms, melting at $115-116^\circ$. *n-Methyltropone methiodide* forms large, colourless, cube-shaped crystals; when treated with sodium hydrogen carbonate, it yields dimethylamine and a liquid, which is probably

a dihydrobenzaldehyde, C_7H_8O . This substance has a sharp odour of oil of bitter almonds, and boils at $70-72^\circ$ (pressure = 14 mm). It appears to be identical with the substance obtained by Einhorn and Eichengrün from anhydroecgonine dibromide (Abstr., 1891, 65).

A. H.

Solubility of Ferments and their Activity in Alcohol. By A. DASTRE (*Compt. rend.*, 1895, **121**, 899—901).—Although relative insolubility in alcohol is generally employed as a means of isolating zymases, and although it has been recognised that some of them are not quite insoluble in even concentrated alcohol, there is at present little definite information on the subject.

The author finds that the digestive ferments and the ferments of the blood are quite insoluble in alcohol of 95%. With aqueous alcohol, the results are different. Trypsin is distinctly soluble in alcohol of from 10 to 25 per cent., but the solubility diminishes rapidly up to 50 per cent., and very rapidly beyond this point, becoming practically nil with 55 per cent. The amylolytic ferment of the pancreas is more soluble, and the solubility is distinct up to 65 per cent. alcohol. With the blood ferments, on the contrary, the solubility ceases to be recognisable with 4 or 5 per cent. alcohol.

Combining these with the previous observations of others, the ferments may be arranged in the following order of increasing solubility:—Blood ferments, emulsin, ptyalin, trypsin, pepsin, the ferment of *gaulleria*, the amylolytic ferment of the pancreas, myrosin.

The ferments remain active in the alcoholic solutions, but their effects are greatly retarded, because the attraction of the alcohol for the water is opposed to the essentially hydrolysing action of the ferments, and many of the digestible substances are insoluble in alcohol. With trypsin, digestive effects were observed with alcohol up to 15 per cent., and with the amylolytic ferment up to alcohol of 20 per cent.

C. H. B.

Glycolysis. By OTTO NASSE and FRIEDRICH FRAMM (*Pflüger's Archiv*, 1896, **63**, 203—208).—Lépine has stated that by the use of dilute sulphuric acid a diastatic can be converted into a glycolytic ferment. These experiments were repeated in the present research, with entirely negative results.

Diastatic ferments turn guaiacum tincture blue; this might account for the disappearance of some of the sugar, for sugar is easily oxidised. This action, however, is not due to the ferment itself, as it does not run parallel with ferment activity. Experiments, however, failed to substantiate the hypotheses.

W. D. H.

The Chemical Nature of Diastase. By THOMAS B. OSBORNE (*J. Amer. Chem. Soc.*, 1895, **17**, 587—603).—The author considers the old method for the preparation of diastase as unsatisfactory, but has used the following method with considerable success.

The proteïds are first separated from the carbohydrates and other substances by saturating the aqueous extract of malt with ammonium sulphate. By this means, the ferment and proteïds are precipitated together; the proteïd, existing as globulin, is then removed by

dialysis, and the albumin and proteoses are separated as far as possible by fractional precipitation with alcohol.

In each case the diastatic power of the product was measured by Lintner's method. Lintner recommends extracting the malt with 20 per cent. alcohol, but the author finds that water is much better.

As a result of his investigations, the author comes to the conclusion that ordinary diastase contains (1) a globulin, (2) an albumin, and (3) probably two forms of proteose, one of which is precipitated by alcohol more readily than the albumin, whilst the other is less readily precipitated.

It is shown that the globulin, which is more readily rendered insoluble than the albumin, can be easily separated from the albumin by repeated precipitation by alcohol and dissolution in water. It is uncertain whether repeated fractional precipitation can be employed to completely separate the albumin from the proteoses. It may be that the proteose is a decomposition product of diastase. The albumin has most of the properties of leucosin, which the author has previously isolated from barley, wheat, and rye. It is also probable that the fermentable properties of diastase are due to the presence of this albumin, as the author finds that diastase containing the greatest percentage of coagulable albumin has the highest fermentable properties. If this albumin is identical with leucosin, it accounts for the fact that extracts of barley, wheat, &c., have a strong diastatic action on starch. The author, however, thinks it more probable that active diastase is a compound of albumin with proteose, and that it breaks up on heating, yielding coagulated albumin, and, further, that free albumin is also present, which has no diastatic power, but is coagulated at the same time.

J. J. S.

Action of Alcoholic Soda on Gelatin and Egg-albumin.

By CARL PAAL and WILHELM SCHILLING (*Chem. Zeit.*, 1895, **19**, 1487—1488).—The "proteic acid," $C_8H_{16}N_2O_6$, obtained by W. Fahrion (*Chem. Zeit.*, **19**, 1000) by acting on silk, glue, &c., with caustic soda, is the hydrochloride of a peptone, such as has been described by Paal (compare Abstr., 1892, 895), and differs in character and composition according to its source. The "metallic salts" described by Fahrion are complicated mixtures of metallic chlorides, peptone hydrochlorides, free peptones, and metallic derivatives of peptones.

A. L.

The Proteids of the Rye Kernel. By THOMAS B. OSBORNE (*J. Amer. Chem. Soc.*, 1895, **17**, 429—448).—Rye meal was exhausted with a solution containing 10 per cent. of sodium chloride, and the extract, after syphoning from the subsided insoluble matters, was freed from salts and globulin by dialysis in river water and by filtration; the solution then contained only those proteids extracted from the seed which were soluble in pure water. These the author shows to be the same as those obtained from wheat meal, namely, an albumin, which he terms *leucosin*, and a proteose. The leucosin is obtained as a coagulum, on warming its aqueous solution to 63—65°, and agrees in composition and properties with that obtained from

wheat. The proteid which is soluble in saline solutions the author shows to be *edestin*, or vegetable vitellin (compare this vol., ii, 210).

Alcohol extracts a proteid, *gliadin*; this is identical with the proteid soluble in alcohol, which has previously been obtained from wheat (compare Abstr., 1893, i, 741). A proteid, which is soluble in dilute potash solution, also occurs in rye meal, but the author was unable to obtain it in a pure state.

The amounts of the various proteids present are given as, gliadin = 4.00, leucosin = 0.43, edestin and proteose = 1.76, proteids insoluble in salt solution = 2.44 per cent. Total = 8.63 per cent. of the meal.

J. J. S.

Method of obtaining Oxyhæmoglobin Crystals. By MAURICE ARTHUS (*Compt. rend. Soc. Biol.*, 1895, 11, 686).—If blood corpuscles dissolved in water are introduced into a dialysing tube, and this is plunged into dilute alcohol (20—25 per cent.), after 24 hours crystals form inside the tube, sometimes large enough to be visible to the naked eye.

W. D. H.

Phrenosin—an immediate Educt from the Brain—and the Products of its Chemolysis by Nitric acid. By JOHN L. W. THUDICHUM (*J. pr. Chem.*, 1896, [2], 53, 49—91).—The author discusses at length the "protagon hypothesis," with special reference to the paper of Kossel and Freytag on the subject (Abstr., 1893, i, 235). He complains that these physiologists have distorted the history of the isolation of nerve educts (compare Abstr., 1882, 235, 537), and have misapplied the name cerebrin to phrenosin. The facts with regard to the "chemolysis" of phrenosin by nitric acid are as follows. At least five products are obtained. (1) Neurostearic acid (Abstr., 1882, 537), which is not identical with stearic acid, as Kossel and Freytag state. (2) *Phrenylin*, a new product, which is insoluble, or very slightly soluble in ether, but soluble in boiling alcohol, from which it separates in the form of a white, microcrystalline mass; it melts gradually between 115° and 130°. This substance yields the oleochole reaction in a hitherto unnoticed manner; the purple colour is not in solution, but belongs to suspended particles, which become colourless when dehydrated by fresh sulphuric acid; the hydrated particles are insoluble in dry chloroform, but dissolve in the hydrated solvent; the nitrogen content of phrenylin and its cleochole reaction indicate that it is a product from the same radicle which yields sphingosine when phrenosine is "chemolysed" with sulphuric acid (*loc. cit.*). Phrenylin is apparently a neutral substance, although it shows a tendency to retain barium, as the cerebrosides do. (3) Mucic acid, which is a product of the oxidation of cerebrose (*loc. cit.*). These three compounds form the chief products of the "chemolysis;" but in addition there were isolated (4) a red-coloured resin acid, and (5) a neutral compound, freely soluble in ether, not capable of combining with baryta, and giving the oleochole reaction.

A. G. B.

Organic Chemistry.

Composition of Marsh Gas. By TH. SCHLOESING, jun. (*Compt. rend.*, 1896, **122**, 398—400).—Sixteen samples of marsh gas, mostly from French coal mines, but some from ditches, contained: methane 55·6 to 96·9 per cent., nitrogen 2·2 to 39·8 per cent., oxygen 0·0 to 0·8, and carbonic anhydride 0·0 to 4·1. As a rule, the proportion of methane is more than 80 per cent. The quantity of oxygen and carbonic anhydride is usually very small, and in most cases, though not in all, these gases have been introduced during the process of collecting. The proportion of nitrogen varies widely, and is sometimes relatively high; it contains the same proportion of argon as atmospheric nitrogen does, and has most probably been derived from the air, the oxygen having been removed by combination with constituents of the coal.

C. H. B.

Action of Bromine on Tertiary Alcohols of the Series $C_nH_{2n+2}O$. By WLADIMIR IPATIEFF (*J. pr. Chem.*, 1896, [2], **53**, 257—287).—The published researches on the chlorination of hydrocarbons of the C_nH_{2n} series show that when such hydrocarbons are of the types $R_2C:CH_2$, $R_2C:CHR$ and $R_2C:CR_2$ they yield unsaturated chlorinated derivatives of the form $C_nH_{2n-1}Cl$, hydrogen chloride being evolved; the hydrocarbons of the types $RHC:CH_2$ and $R'HC:CHR$, however, yield dichlorides, $C_nH_{2n}Cl_2$, without separation of hydrogen chloride. The bromination of the ethylenes appears to produce a dibromide in every case, although Faworsky has shown that the dibromide is by no means always the sole product.

The work of Etard (*Abstr.*, 1892, 809) has established the similarity between the action of chlorine and that of bromine on primary and secondary alcohols, but the behaviour of tertiary alcohols with bromine has received but little notice. The author finds that when dimethylethylcarbinol is left in contact with bromine (1 mol.) at the normal, or at slightly lower, temperature, no action occurs for some hours, but presently it begins and proceeds so rapidly that the mixture explodes. By heating the carbinol at 50—56°, the action takes place sufficiently rapidly for each drop of bromine to disappear as it falls from the dropping-funnel, and the bromination may be conducted with safety. After all the bromine has been added, and the flask has been left at rest for a day, two layers have formed, the lower of which is the brominated product; it is washed with sodium carbonate solution, dried, and fractionally distilled at 16 mm. pressure. The chief product (77 per cent.) distils at 64—66°, and is amylene dibromide, $CMe_2.CBr.CHMeBr$; its sp. gr. = 1·7005 at 0°/0°; and its constitution is settled by the fact that when heated with lead oxide and water it yields methyl isopropyl ketone, and further by its behaviour with alcoholic potash, by which it may be successively converted into bromotrimethylethylene $CMe_2.CMeBr$ (b.p. 118°; sp.gr.,

= 1.3073 at 0°/0°), and dimethylisoallylene, $\text{CMe}_2\text{:C:CH}_2$ (b. p. 39.5—41°); it must contain a small proportion of the dibromide,



for a little methylethylacetaldehyde is found in the product of both the above reactions. A tertiary amylic bromide and a tribromopentane are the other products of the bromination of dimethylethylcarbinol.

Contrary to the statement of Jawein (*Annalen*, 195, 255), the author finds that dimethylpropylcarbinol can be prepared in quantity (50 per cent.) by Butleroff's method from zinc methide and butyric chloride. It was treated with bromine in the manner described above and was found to yield small proportions of a tertiary hexylic bromide and tribromohexane, but chiefly (70 per cent.) hexylene dibromide, $\text{CMe}_2\text{Br}\cdot\text{CHBr}\cdot\text{CH}_2\text{Me}$ (sp. gr. = 1.6196 at 0°/0°) together with a little of the dibromide $\text{CH}_2\text{Br}\cdot\text{CMeBr}\cdot\text{CH}_2\cdot\text{CH}_2\text{Me}$. The first of these two dibromides was converted into a bromohexylene (b. p. 138—141°; sp. gr. = 1.2491 at 0°/0°), and a hydrocarbon, C_6H_{10} (b. p. 71—73°, uncorr.; sp. gr. = 0.73033 at 0°/0°), by treatment with alcoholic potash.

Three holic derivatives are similarly obtained by brominating triethylcarbinol, namely a tertiary hexylic bromide, a heptylene dibromide (55 per cent.) and a tribromoheptane. It seems, therefore, that this is the general course of the action of bromine on tertiary alcohols, the proportion which the three products bear to each other being dependent on the temperature at which the action takes place.

The paper contains details of the method which the author has found most suitable for preparing considerable quantities (300—400 grams) of zinc methide from zinc and methylic iodide at one operation.

A. G. B.

Action of Nitric acid on Potassium Cobalticyanide.

By C. LORING JACKSON and ARTHUR M. COMEY (*Ber.*, 1896, 29, 1020—1022).—When a concentrated solution of potassium cobalticyanide is boiled with an equal volume of strong nitric acid, it becomes coloured red after some minutes and then forms a semi-solid gelatinous mass, which dissolves slowly in water at 60° when it has been freed from impurities by washing. This substance after drying in a vacuum has the composition, $\text{KH}_2\text{Co}_3(\text{CN})_{11} + \text{H}_2\text{O}$. The amorphous mass obtained by the evaporation of its solution in water, is converted into a red powder by treatment with cold water. The solution has acid properties and yields precipitates with the solutions of various metallic salts. The silver salt is a pale red, amorphous mass of the formula $\text{Ag}_3\text{Co}_3(\text{CN})_{11} + \text{H}_2\text{O}$, whilst the barium salt has the formula $\text{BaHCo}_3(\text{CN})_{11} + 1\frac{1}{2}\text{H}_2\text{O}$. The free cobaltocobalticyanic acid is prepared in a similar manner from cobalticyanic acid and closely resembles the potassium salt, but is less stable. Potassium ferricyanide appears to yield a somewhat similar substance when it is treated in the same manner, but this has not yet been carefully examined.

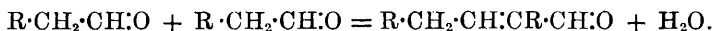
A. H.

New Mode of Formation of Nitroprussides. By C. MARIE and R. MARQUIS (*Compt. rend.*, 1896, 122, 473—474).—When potassium ferricyanide in aqueous solution is acted on by nitrous acid liberated from sodium nitrite by carbonic anhydride, it is completely converted into the ferrocyanide, and only traces of nitroprusside are formed. On the other hand, when potassium ferrocyanide is treated in the same way, it is largely converted into the nitroprusside, the reaction being limited by the reversing action of the alkali carbonate that is formed. With calcium ferrocyanide, inert calcium carbonate is formed, and the change into nitroprusside is complete. C. H. B.

Methylic Alcohol, Acetic acid, and Carbon from various Woods. By ERNEST BARILLOT (*Compt. rend.*, 1896, 122, 469—471).—Fractionation of the crude product of the destructive distillation of various woods shows that for 100 kilos. of wood the yield of acetic acid varies from 3.72 to 6.40 kilos., of methylic alcohol from 1.27 to 2.15 litres, and of charcoal from 20.62 to 26.0 kilos. A mixture of oak, beech, and hornbeam gave the best yield of the alcohol. White woods are, as a rule, to be avoided for the production of charcoal.

C. H. B.

Constitution of Glycols formed by the Action of Caustic Potash on Aldehydes. By ADOLF LIEBEN (*Monatsh.*, 1896, 17, 68—75).—The constitution assigned by Fosseck (*Compare Abstr.*, 1884, 37) to the glycols obtained by acting on mixtures of isobutyric with other aldehydes, is not that which is to be expected if the rule of Lieben and Zeisel be applied. The latter requires the initial production of an unsaturated aldehyde in the following manner :



In the case of isobutaldehyde, where the tertiary carbon attached to the aldehydic group is incapable of yielding an unsaturated compound in the above fashion, a hydroxy-aldehyde or aldol should be the initial product, the subsequent production of a glycol resulting from the reducing action of the caustic potash.

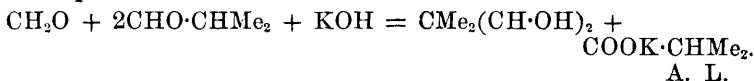
In order to decide between the two views, experiments have been undertaken with the object of ascertaining if glycols are produced when aldehydes other than those of the isobutyric type are used, and the results are in favour of the latter view.

The author discusses the experiments of Just and Franke (compare the two following abstracts) in relation to the above hypotheses, and mentions that similar experiments are being made in which caustic soda is substituted for potash. A. L.

Action of Alcoholic Potash on a Mixture of Formaldehyde and Isobutaldehyde. By ALEXANDER JUST (*Monatsh.*, 1896, 17, 76—84).—The action of alcoholic potash on a mixture of isobutaldehyde and formaldehyde results in the production of isobutyric acid and a glycol, $C_5H_{12}O_2$. The latter is doubtless identical with the glycol obtained by Apel and Tollens (*compare Abstr.*, 1894, i, 353) by the action of calcium hydroxide on the same mixture of aldehydes ;

it is very hygroscopic, dissolves readily in water, ether, alcohol, chloroform, and hot benzene, crystallising from the latter in beautiful needles; it boils at 206° under 747 mm. pressure, and melts at 127° . The *diacetate* boils at 212° under 740 mm. pressure. The glycol, on oxidation with potassium permanganate, yields acetone and a mixture of two acids, one dimethylmalonic acid, and the other in all probability hydroxytrimethylacetic acid, as the former is obtained from it by oxidation.

From these results it is seen that the above action may be expressed by the equation



Action of Alcoholic Potash on Isobutaldehyde. By ADOLF FRANKE (*Monatsh.*, 1896, **17**, 85—101).—The glycol obtained by Fossek (*Abstr.*, 1882, 1279) by the action of alcoholic potash on isobutaldehyde, when treated with cold, concentrated sulphuric acid, yields only a small quantity of oil, the bulk of the product consisting of a *glycolic hydrogen sulphate*, which may be isolated by means of its *barium* salt. The latter crystallises in silky, colourless needles, dissolves readily in water, decomposes at 70 — 80° with production of barium sulphate, and, when heated with somewhat dilute sulphuric acid, yields the oily product described by Fossek and Swoboda (see *Abstr.*, 1891, 31). The latter may be directly prepared from the glycol by the action of boiling dilute sulphuric acid, and, as stated by its discoverers, may be separated by distillation into a low-boiling and a high-boiling portion of the compositions, $\text{C}_8\text{H}_{16}\text{O}$ and $\text{C}_{16}\text{H}_{32}\text{O}_2$ respectively. The low-boiling portion is a saturated compound, does not interact with acetic anhydride, phenylhydrazine or hydroxylamine, and does not combine with water at 130 — 140° ; it is therefore an oxide, comparable with ethylenic oxide, inexplicable by means of Fossek's formula for the glycol.

The glycol is slowly oxidised by cold, dilute potassium permanganate, yielding diisopropyl ketone, $\text{CO}(\text{CMe}_2)_2$, and the hydroxy-acid $\text{C}_8\text{H}_{16}\text{O}_3$, obtained by Fossek (*loc. cit.*). The latter yields diisopropyl ketone on oxidation, and is therefore trimethyl-2:2:4-pentanol-3-oic acid, $\text{COOH}\cdot\text{CMe}_2\cdot\text{CH}(\text{OH})\cdot\text{CHMe}_2$; hence the glycol is trimethyl-2:2:4-pentane-1:3 diol, $\text{OH}\cdot\text{CH}_2\cdot\text{CMe}_2\cdot\text{CH}(\text{OH})\cdot\text{CHMe}_2$.

The oxide, $\text{C}_8\text{H}_{16}\text{O}$, is oxidised by dilute acid permanganate to an acid, either acetic or dimethylmalonic acid, and a volatile *substance*, $\text{C}_{10}\text{H}_{14}\text{O}_2$, which separates from ether in long, prismatic, channelled crystals, is volatile in steam, melts at 42° , and boils without decomposing at 205° ; when boiled with calcium hydroxide, it yields a *calcium* salt, $(\text{C}_8\text{H}_{15}\text{O}_3)_2\text{Ca}$, forming a colourless, crystalline mass, and is therefore the lactone of a γ -hydroxy-acid, $\text{C}_8\text{H}_{16}\text{O}_3$, and has the

constitution $\begin{array}{c} \text{CH}_2\cdot\text{CMe}_2 \\ | \\ \text{CMe}_2\cdot\text{CO} \end{array} > \text{O}$. The oxide, whence the lactone is derived, is therefore, in all probability, a 1:4-oxide of the structure $\begin{array}{c} \text{CH}_2\cdot\text{CMe}_2 \\ | \\ \text{CMe}_2\cdot\text{CH}_2 \end{array} > \text{O}$, produced from the 1:3-glycol by the initial production,

under the influence of the sulphuric acid, of a 3:4-unsaturated alcohol.

The oil of high boiling point, $C_{16}H_{32}O_2$, obtained simultaneously with the above oxide, proves to be an ether, being decomposed by fuming hydrobromic acid at 100° , with production of brominated compounds which readily lose hydrogen bromide on distillation, whilst by the action of dilute sulphuric acid at 100° , it is partially decomposed, the oxide, $C_8H_{16}O$, being formed. It is probably, therefore, a ditetra-methyltetramethylene dioxide. A. L.

Condensation of Formaldehyde with Anhydro-enneaheptitol.

By M. APEL and O. WITT (*Annalen*, 1896, **290**, 153—155; compare this vol., i, 115).—*Anhydro-enneaheptitol diformal*, $C_{11}H_{18}O_6$, is obtained from formaldehyde and anhydro-enneaheptitol under the influence of hydrochloric acid; it occurs in two modifications, which melt at 165° and 207° respectively. The same *acetate* is produced from both sources, and melts at 107° . M. O. F.

Galactitol, from Yellow Lupin Seed. By C. HEINRICH L. RITTHAUSEN (*Ber.*, 1896, **29**, 896—899).—*Galactitol*, $C_{19}H_{18}O_7$, is obtained by extracting lupin seed with dilute alcohol (80 per cent.), evaporating the solution to dryness, and purifying the residue from fat, lupinine, and lupinidine; it crystallises in thin colourless, hexagonal, hemihedral plates belonging to the rhombic system, $a : b : c = 0.5068 : 1 : 0.7332$; $\beta = 1.52$; the compound softens at 138° , melts at 140 — 142° , is tasteless, and optically inactive. The yield is 1.05 per cent. of the seed employed. When hydrolysed by means of dilute sulphuric acid, galactitol yields more than 60 per cent. of galactose, which was fully identified. J. B. T.

Action of Fuming Nitric acid on Xylose and on Arabinose.

By RICHARD BADER (*Chem. Zeit.*, 1895, **19**, 1851; compare this vol., i, 335).—The author has further examined the white, hygroscopic mass obtained on treating xylose with fuming nitric acid, which was thought to be xylotrihydroxyglutaric anhydride. The mass usually contains 0.2—1.5 per cent. of nitrogen due to impurities; it was found impossible to obtain either the acid itself, or its ammonium or silver salt, in a state of purity, from the anhydride; by careful working, however, a barium salt was obtained, which yielded numbers agreeing with those required for barium trihydroxyglutarate.

Arabinose treated in the same way yields arabinotrihydroxyglutaric anhydride, but none of the derivatives of the acid could be obtained in a pure form. J. J. S.

Isomaltose. By ED. JALOWETZ (*Chem. Zeit.*, 1895, **19**, 2003; compare Ling and Baker, *Trans.*, 1895, 704; Brown and Morris, *ibid.*, 709; H. Ost, *Chem. Zeit.*, 1895, **19**, 1501; and Ulrich, this vol., i, 335).—The author shows that pure maltose, when mixed with varying quantities of dextrin, yields osazones, which not only differ in melting point, but also in their general appearance and crystalline form. With equal quantities of maltose and dextrin an osazone is obtained,

which melts at 150—155°, but the melting point alters after several recrystallisations.

These results agree with those of the authors mentioned, and speak against the existence of Lintner's isomaltose. J. J. S.

Behaviour of Basic Lead Acetate towards Sugar Solutions.

By HANNO SVOBODA (*Zeits. Ver. Rübenzucker-Ind. Deut. Reichs.*, 1896, 46; Heft 481, 29 pages).—When 20 per cent. sugar solutions are treated for 24 hours with lead acetate (1 vol.), the solutions become coloured, as follows: maltose, red; galactose, orange; levulose, yellow; dextrose, bright yellow; lactose, yellowish; there is also a decrease in polarisation, most in the case of galactose (53 per cent.), least with maltose; cane sugar, and raffinose are not decomposed, but when more lead oxide than usual is present, raffinose is precipitated. The amount of lead oxide in solution, to which the action is due, may be estimated by treating with excess of titrated sulphuric acid for three hours, and then titrating back with sodium hydroxide.

As regards the effect of lead acetate on the rotatory power of sugars, that of cane sugar is at first slightly diminished, then raised, and, finally, diminished. The rotatory power of maltose is slightly lessened, that of raffinose, lactose, galactose, and levulose considerably diminished, according to the amount of lead acetate added. When the lead solution is slightly acidified with acetic acid, a slight alteration of rotatory power is produced. Addition of increasing amounts causes, with (1) cane sugar and dextrose, a slight constant increase; (2) levulose, at first a slight diminution, then an increase; (3) lactose, maltose, galactose, and raffinose, a slight diminution of rotatory power. The changes in rotatory power are due to the formation of soluble lead sucates; these compounds are precipitated by much alcohol, and contain lead oxide, 66·5—73·6; sugar, 10·9—16·7; and acetic anhydride, 13·6—16·5 per cent. They are not true sucates, as they contain acetic acid, but compounds of sugar with basic lead acetate. Beythien and Tollen's trilead raffinosate contains 10 per cent. of acetic anhydride (*Zeits. Ver. Rübenzucker-Ind.*, 1889, 748 and 906; Abstr., 1890, 580). Aqueous solutions of the sucates behave, as regards rotation, very similarly to the sugar solutions containing lead acetate.

A mixture of dilute lead acetate solution and an equal bulk of 3 per cent. ammonia precipitates sugar from aqueous solutions. The cane sugar precipitate is free from ammonia, and contains 2·85 per cent. of acetic anhydride.

The filtrate obtained from a solution of lead acetate after treatment with sufficient baryta, strontia, or lime to decompose the neutral lead acetate, precipitates sparingly soluble lead sucates from sugar solutions. Magnesium hydroxide does not have this effect, but a magnesia precipitant is obtained by digesting magnesium acetate (20 grams) in water (100 c.c.) with litharge (20 grams). The precipitating power of these solutions is proportional to the amount of basic lead oxide present; and this depends on the strength of the base, being greatest in the case of magnesia, least with baryta. Zinc lead acetate does not precipitate more than lead

acetate. The precipitates are free from baryta, strontia, &c., and contain, besides sugar and lead, acetic acid (3.4—4.7 per cent.). The magnesia lead acetate solution (9 grams of lead oxide per c.c.) precipitates, from 20 per cent. solutions, 75 to 100 per cent. of sugar, according to the nature of the sugar, and thus forms a method for isolating and identifying different sugars.

The precipitation of sugar from solutions containing sulphates, chlorides, &c., on adding lead acetate, is explained thus:—With sugars, basic lead acetate forms various sucates which dissolve readily in lead acetate, but only sparingly in water. Salts which react with lead acetate to form insoluble lead compounds precipitate the sucates by precipitating the solvent. N. H. J. M.

Preparation of Fatty Amines. By AUGUSTE TRILLAT (*Bull. Soc. Chim.*, 1895, [3], 13, 689—692).—The author does not agree with the conclusions of Brochet and Cambier (*Abstr.*, 1895, i, 325) that in the preparation of methylamine from formaldehyde and ammonium chloride the presence of a reducing agent does not hasten the reaction. By working with a mixture of formaldehyde, ammonia, and hydrochloric acid in the presence of a small quantity of zinc, he has been enabled to obtain the methylamine in the space of a few minutes. Ethylamine results from the reduction of aldehydammonia, and not pyridine bases as stated by the above-mentioned investigators.

J. F. T.

Reduction of Methylnitramine and Ethylnitramine. By JOHANNES THIELE and CARL MEYER (*Ber.*, 1896, 29, 961—963).—Thiele and Lachman have suggested (this vol., i, 207) that when reduced, methylnitramine is first converted into nitrosomethylamine and then into diazomethane. β -Methoxynaphthalene is produced by the interaction of methylnitramine, β -naphthol, and aluminium in alkaline solution, thus indicating the production of diazomethane; but the isolation of this from aqueous solution is practically impossible. When reduced as above, without β -naphthol, the liquid on acidifying evolves nitrogen (about two-sevenths of the theoretical), and rapidly reduces metallic salts. Nitrous acid is only present in traces. When reduced by means of hydrochloric acid and zinc dust, methylnitramine is converted into hydrazine, methylhydrazine, and methylamine. The yield of methylhydrazine is poor. Ethylnitramine, under the same conditions, gives ethylhydrazine, the yield being slightly better. Methylnitramine is obtained from dinitrodimethyloxamide which is readily prepared by mixing dimethyloxamide (20 grams) with common nitric acid (50 c.c.), adding distilled sulphuric acid (100 c.c.), and treating the crystals with ice. The yield is 99—100 per cent. of the theoretical.

J. B. T.

Oxidation of Crotonaldehyde. By ER. CHARON (*Compt. rend.*, 1896, 122, 533—535).—Crotonaldehyde, prepared by the methods of Lieben and of Newbury and Orndorff, does not appear to have a definite boiling point; it therefore seemed interesting to ascertain whether the product was a homogeneous substance, or whether it was a mixture of the two possible stereoisomerides.

The aldehyde was, therefore, oxidised by means of silver oxide, and was found to give the acid melting at 71° ; even on separating the aldehyde into two fractions and oxidising them separately, the same acid was in each case produced, the yield being 90 per cent. of the theoretical. The acid melting at 71° was also obtained on allowing the aldehyde to oxidise slowly in the air.

J. F. T.

Disubstituted Amidoacetones. By RICH. STOERMER and W. POGGE (*Ber.*, 1896, **29**, 866—874; compare *Abstr.*, 1895, 681).—*Dipropylamidoacetone*, $\text{NPr}_2\text{CH}_2\text{COMe}$, boils at 188° , and has the sp. gr. 0.8337 at 14° . The *hydrochloride* forms white, lustrous plates; the *platinochloride* melts at 175 — 176° , the *aurochloride* at 95 — 96° . The *methiodide* crystallises in white needles melting at 234° ; the *oxime* is an oil which could not be obtained crystalline, and the *hydrazone* is also an oil. The *semicarbazone* is a microcrystalline powder melting at 110° .

Methylpropylamidoacetone is formed by the distillation of the quaternary hydroxide obtained from the methiodide of the foregoing base. It boils at 129° , has a smell resembling that of peppermint, and forms a *platinochloride* which melts at 169 — 170° .

Diisobutylamidoacetone boils at 206 — 207° , and becomes yellow when kept; its sp. gr. is 0.8735 at 15° . The *platinochloride* melts at 176 — 177° , the *aurochloride* at 145° , the *hydrochloride* at 276° , the *hydrobromide* at 279° , and the *hydriodide* at 281° . The last three salts are all soluble in water, but are not hygroscopic. The *methiodide* forms small, lustrous crystals, and melts at 288° , whilst the *semicarbazone* melts at 132° . *Methylbutylamidoacetone* boils at 154 — 155° ; the *platinochloride* melts at 149 — 150° . *Diisoamylamidoacetone* boils at 219 — 220° , and has the sp. gr. 0.8911 at 17° . The *hydrochloride* melts above 290° ; the *platinochloride* and *aurochloride* could not be prepared, since the solutions of these chlorides are immediately reduced by the base. The *methiodide* melts above 290° . The *oxime* crystallises in lustrous, white plates; the *semicarbazone* melts at 166° .

Methylamylamidoacetone boils at 175 — 176° ; the *platinochloride* melts at 139 — 140° . When the methiodide of this base is converted into the hydroxide and distilled, dimethylamidoacetone is formed.

The solubility of the bases and their hydrochlorides in water decreases as the molecular weight rises.

A. H.

Melting and Solidifying Points of some Fatty acids. By GUSTAVE MASSOL (*Bull. Soc. Chim.*, 1895, [3], **13**, 758—759).—By the use, for temperatures down to -55° , of methylic chloride, and below this of a mixture of solid carbonic anhydride and ether, the following constants have been determined.

	Melting point.	Solidifying point.
Propionic acid	-36.5°	-40°
Normal valeric acid ...	-58.5	-64
Isobutyric acid.....	-79.0	-82
Isovaleric acid	-51.0	-57

J. F. T.

Existence of a Sulphur Compound in Cotton-seed Oil. By J. DUPONT (*Bull. Soc. Chim.*, 1895, [3], 13, 696—697).—The author considers the well-known action of cotton-seed oil on silver nitrate solutions, not to be due to reduction, and therefore deposition of metallic silver, but to the presence of a sulphur compound in the oil, and the consequent precipitation of silver sulphide.

On distillation with steam and extraction of the distillate with ether, cotton-seed oil yields a powerfully smelling product, which, when oxidised with nitric acid and treated with barium chloride, gives a copious precipitate of barium sulphate.

In this manner, 5 grams of cotton-seed oil were found to contain 0.021 gram of sulphur. The compound is, however, only slightly volatile, for although this sample had been distilled with a quantity of steam corresponding with 2 litres of water, yet the residual oil still gave the silver nitrate reaction. J. F. T.

Halogen Substitution Derivatives of Ethylic Acetoacetate. By MAX CONRAD (*Ber.*, 1896, 29, 1042—1048.) With L. SCHMIDT.—When ethylic acetoacetate, dissolved in carbon bisulphide, is treated with bromine at the ordinary temperature, the mixture allowed to remain, and then poured into water, the product consists entirely of ethylic γ -bromacetoacetate. If, on the other hand, the mixture is immediately freed from hydrobromic acid by agitation with water, a mixture of the α - and γ -bromo-compounds is obtained. This probably accounts for the results obtained by Nef (*Abstr.*, 1892, 140) and other chemists. Ethylic α -bromacetoacetate, on the other hand, is obtained pure by the action of bromine on ethylic acetoacetate mixed with double its volume of water, and cooled by ice. The α -compound is not converted into the γ -derivative by distillation under reduced pressure, and does not yield ethylic succinosuccinate when treated with sodium ethoxide.

Ethylic α -chloracetoacetate does not appear to be converted into the γ -compound even when left in contact with hydrogen chloride for a protracted period. *Ethylic $\alpha\alpha$ -chlorobromacetoacetate* is formed when chlorine is passed into ethylic α -bromacetoacetate, and is a colourless oil. Ammonia converts it into chlorobromacetamide, which melts at 117°. Ethylic $\alpha\alpha$ -dibromacetoacetate reacts with 2 mols. of thiocarbamide to form ethylic μ -amidomethylthiazolecarboxylate.

With ANTON KREICHGAUER.—The behaviour of methylic methylacetoacetate towards bromine is similar to that of ethylic acetoacetate, the γ -bromo-compound being obtained when the product is allowed to remain in contact with hydrogen bromide for some time. It is a colourless oil, the vapour of which irritates the eyes. When heated for some hours on the water bath, it is converted into tetric acid. With thiocarbamide, it yields *methylic μ -amidothiazylpropionate*,
$$\text{COOMe} \cdot \text{CHMe} \cdot \text{C} \begin{array}{l} \nearrow \text{CH} \cdot \text{S} \\ \searrow \text{N} = \text{C} \cdot \text{NH}_2 \end{array}$$
, which crystallises in colourless prisms, and melts at 130°.

Methylic α -bromomethylacetoacetate is formed when the bromination is carried out at 0° and in presence of water. It is an oil which does

not react with thiocarbamide. When kept, it gradually changes into the γ -derivative.

A. H.

Relation between Derivatives of Ricinoleic and Oleic acids.

By OTTO BEHREND (*Ber.*, 1896, **29**, 806—809).—*Bromoketostearic acid*, $\text{CH}_3\cdot[\text{CH}_2]_5\cdot\text{CHBr}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}\cdot[\text{CH}_2]_7\cdot\text{COOH}$, can be prepared in the same way as chloroketostearic acid (*Abstr.*, 1895, i, 647); it melts at 55° , and, when recrystallised from acetic acid or alcohol, is slowly reconverted into hydroxyketostearic acid, hydrogen bromide being given off.

Chloroketostearic acid is reduced by hydriodic acid at 180° to stearic acid. It is reduced by zinc and hydrochloric acid at 80 – 90° to a *ketostearic acid*, which melts at 83° , and must have the constitution $\text{CH}_3\cdot[\text{CH}_2]_8\cdot\text{CO}\cdot[\text{CH}_2]_7\cdot\text{COOH}$, for it yields an oxime, and this undergoes the Beckmann transformation, yielding an amide (possibly a mixture of stereoisomeric varieties, for it melted at 75 – 85°) which on hydrolysis gave nonylamine, $\text{CH}_3\cdot[\text{CH}_2]_8\cdot\text{NH}_2$, and azelaic acid, $\text{COOH}\cdot[\text{CH}_2]_7\cdot\text{COOH}$, and also capric and amidocaprylic acids, $\text{CH}_3\cdot[\text{CH}_2]_8\cdot\text{COOH}$ and $\text{NH}_2\cdot[\text{CH}_2]_7\cdot\text{COOH}$. This ketostearic acid is isomeric with that prepared by Baruch from stearolic acid (*Abstr.*, 1894, i, 170).

C. F. B.

Constitution of Behenoxylic and Stearoxylic acids.

By A. SPIECKERMANN (*Ber.*, 1896, **29**, 810—813).—Ketoketoximebehenic acid (*Abstr.*, 1895, i, 208), which melts, when pure, at 85 – 86° , undergoes the Beckmann transformation, and yields *pelargylamidobrassylic acid*, $\text{CH}_3\cdot[\text{CH}_2]_7\cdot\text{CO}\cdot\text{NH}\cdot\text{CO}\cdot[\text{CH}_2]_{11}\cdot\text{COOH}$. This melts at 116° , and can be hydrolysed into ammonia and pelargonic and brassylic acids, $\text{CH}_3\cdot[\text{CH}_2]_7\cdot\text{COOH}$ and $\text{COOH}\cdot[\text{CH}_2]_{11}\cdot\text{COOH}$. Behenoxylic acid must, therefore, be $\text{CH}_3\cdot[\text{CH}_2]_7\cdot\text{CO}\cdot\text{CO}\cdot[\text{CH}_2]_{11}\cdot\text{COOH}$, and, as we should expect from such a compound, it does actually yield, with orthophenylenediamine, a quinoxaline (*octylquinoxaline-dodecoic acid*, $\text{C}_6\text{H}_4\cdot\begin{smallmatrix} \text{N}:\text{C}\cdot[\text{CH}_2]_7\cdot\text{CH}_3 \\ | \\ \text{N}:\text{C}\cdot[\text{CH}_2]_{11}\cdot\text{COOH} \end{smallmatrix}$, melting at 45°). Behenoxylic acid melts at 95° when pure; the acid obtained as a bye-product in its preparation, and formerly supposed to be behenic acid, has now been identified as arachidic acid.

Stearoxylic acid is shown in a similar manner to have the constitution $\text{CH}_3\cdot[\text{CH}_2]_7\cdot\text{CO}\cdot\text{CO}\cdot[\text{CH}_2]_7\cdot\text{COOH}$, for it yields a *ketoketoxime acid*, melting at 76 – 81° , and this undergoes the Beckmann transformation into *pelargylamidoazelaic acid*,

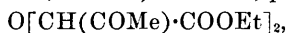


which can be hydrolysed to ammonia, pelargonic acid, and azelaic acid, $\text{COOH}\cdot[\text{CH}_2]_7\cdot\text{COOH}$.

C. F. B.

Derivatives of Ethylic Acetoacetate.

By CARL BOETTINGER (*Arch. Pharm.*, 1896, **234**, 87—91) —An oil, probably



was prepared in the following manner. Strong sulphuric acid (several drops) is added at intervals of a day to a mixture of equal weights of glyoxylic acid and ethylic acetoacetate, until 7 c.c. has been added in all; after 10 days ether is added, and the solution washed with water. The ethereal solution is evaporated, and the residual oil is shaken with water; this aqueous solution leaves a yellow syrup when evaporated, and this is completely soluble in cold water; the solution reduces ammoniacal silver nitrate, and contains an acid which has not been isolated in a pure form. The oil remaining undissolved by the water is heated with a solution of lead acetate, and the product extracted with ether, whereby a white lead salt is obtained which gives a vapour smelling of ethylic acetate when heated with strong sulphuric acid; a yellow barium salt is formed when the oil is treated with baryta water. The oil is viscid, colourless, and difficultly solidified; when heated, it gives a pungent vapour; aqueous ammonia hardly dissolves it at all, and in water it is insoluble; with bromine, it yields a product which is insoluble in dilute soda, but gives an odour of carbylamine when heated with aniline and sodium hydroxide. With phenylhydrazine, a compound is formed. Carbonic anhydride, alcohol, oxalic acid, and an aromatic compound were detected among the products of heating the oil with baryta in a sealed tube.

A. G. B.

Sodium Glyoxylate. By CARL BOETTINGER (*Arch. Pharm.*, 1896, **234**, 91).—*Sodium glyoxylate*, $\text{NaC}_2\text{H}_3\text{O}_4$, is precipitated when sodium ethoxide is added to an alcoholic solution of glyoxylic acid.

A. G. B.

Derivatives of Glycollic acid. By CARL BOETTINGER (*Arch. Pharm.*, 1896, **234**, 158—160).—*Orthoanisidine glycollate*, prepared by heating a mixture of glycollic acid and orthoanisidine in molecular proportion, crystallises in nearly colourless, six-sided tables, melts at 77—78°, and dissolves easily in cold water; strong nitric acid dissolves it to a dirty violet coloured solution.

Glycollic orthoanisidide is obtained by heating crystallised glycollic acid (1 part) with orthoanisidine ($1\frac{1}{2}$ part) at 150—160°; it crystallises in small, silvery laminae, melts at 102—103°, and dissolves sparingly in water, but freely in hot ethylic and methylic alcohols.

Paranisidine glycollate crystallises in needles, melts at 85—86°, and dissolves easily in water and warm alcohol; it colours strong nitric acid blue, the colour quickly changing to violet, and becoming red on dilution.

Glycollic paranisidide crystallises in long, soft needles, melts at 97°, and is very slightly soluble in cold water, but easily in warm methylic alcohol; strong nitric acid dissolves it to a yellowish-red liquid, the colour quickly changing to yellow.

Paraphenetidine glycollate forms massive, transparent crystals, melts at 95—96°, and dissolves easily in cold water; in strong nitric acid it dissolves with a violet colour, passing into blue.

Glycollic paraphenetidide crystallises in long, white, soft, felted needles, melts at 159—160°, and dissolves in ethylic and methylic alcohols.

A. G. B.

Stereoisomeric Thiodilactylic acids. By JOHAN M. LOVÉN (*Ber.*, 1896, **29**, 1132—1136).—One inactive thiodilactylic acid, $S(CHMe\cdot COOH)_2$, has been previously described; it crystallises in monoclinic prisms, $a : b : c = 1.4288 : 1 : 1.0105$; $\beta = 75^\circ 49' 45''$, melts at 125° , is soluble in 6.67 parts of water at 14° , and in all proportions at 100° . The sp. gr. of a saturated solution at $14^\circ = 1.033$; $K = 0.049$. The amide crystallises in long, asbestos-like needles, melts at 18° , and dissolves in 19.46 parts of water. From the mother liquor of the acid, an isomeric inactive acid is deposited in needles; these, when further purified, change to prisms, probably belonging to the triclinic system; the separation of the acids is effected mechanically, or by fractional crystallisation from water. It melts at 109° , and dissolves in 2.438 parts of water at 14° . The sp. gr. of a saturated aqueous solution $= 1.082$ at 14° ; $K = 0.044$. The amide crystallises in short, transparent prisms, and is less soluble than the isomeric compound, dissolving in 47.08 parts of water at 18° . The acids differ from thiolactylhydracrylic acid (compare following abstract), and are formed both from bromopropionic acid and from chloropropionic acid, they therefore appear to be stereoisomerides, but it is impossible to say which is the racemic and which the meso-form, as all attempts to resolve them into active components have been unsuccessful. J. B. T.

Thiodihydracrylic acid and β -Sulphonedipropionic acid. By JOHAN M. LOVÉN (*Ber.*, 1896, **29**, 1136—1139).—*Thiodihydracrylic* [*thiodipropionic*] acid, $S(CH_2\cdot CH_2\cdot COOH)_2$, is prepared by the interaction of sodium hydrogen sulphide and sodium β -iodopropionate in concentrated aqueous solution; it is also formed in small quantity in the preparation of thiohydracrylic acid; it crystallises from water in long, pearly, lustrous, rhombic plates, melts at 128° , and dissolves in 29.6 parts of water at 26.1° ; $K = 0.0078$. The salts are not characteristic. The *barium* salt forms nodular aggregates, but when the solution is quickly evaporated, it becomes gummy.

β -Sulphonedipropionic acid, $SO_2(CH_2\cdot CH_2\cdot COOH)_2$, is obtained by the oxidation of the preceding compound by means of potassium permanganate or bromine water; it crystallises in lustrous, hexagonal plates, melts at 210° , and dissolves in 441 parts of water at 26.8° ; $K = 0.024$. The *ethylic* salt crystallises in voluminous groups of slender, silky, lustrous needles, melts at 82.5° , and is readily soluble in hot, but not in cold, alcohol. It does not react with sodium ethoxide and ethylic iodide at 120° . Dithiodihydracrylic acid is soluble in about 1000 parts of water at the ordinary temperature. J. B. T.

Unsymmetrical Homologues of Thiodiglycollic acid and of Sulphonediacetic acid. By JOHAN M. LOVÉN (*Ber.*, 1896, **29**, 1139—1143).—Unsymmetrical homologues of thiodiglycollic acid, corresponding with unsymmetrical ethers, are prepared by the interaction of the neutral sodium salts of mercapto-acids and those of haloïd fatty acids in concentrated aqueous solution. *Thioglycolhydracrylic* [*acetic- β -thiopropionic*] acid, $COOH\cdot CH_2\cdot CH_2\cdot S\cdot CH_2\cdot COOH$, is

prepared from sodium thiohydracrylate and sodium chloracetate in presence of soda, and may also be obtained from sodium thioglycollate and sodium β -iodopropionate. Under these conditions the bivalent sulphur is not asymmetric. The acid is crystalline, stable in air, and melts at 94° ; $K = 0.025$. *Thiolactylglycollic* [*acetic- α -thiopropionic*] acid, $\text{COOH}\cdot\text{CHMe}\cdot\text{S}\cdot\text{CH}_2\cdot\text{COOH}$, prepared from sodium thiolactate and sodium chloracetate, is readily soluble, crystallises in plates, and melts at $87\text{--}88^\circ$; $K = 0.048$. *Thiolactylhydracrylic* [*$\alpha\beta$ -thiodipropionic*] acid, $\text{COOH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{S}\cdot\text{CHMe}\cdot\text{COOH}$, from sodium thiolactate and sodium β -iodopropionate, is stable in air, and crystallises in prisms melting at $72\text{--}73^\circ$; $K = 0.021$.

The above acids are readily oxidised to sulphone acids by means of potassium permanganate (2 per cent.). *Acetic- β -sulphonepropionic* acid, $\text{COOH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{SO}_2\cdot\text{CH}_2\cdot\text{COOH}$, crystallises in lustrous plates, melts at $154\text{--}155^\circ$, and is stable in air; $K = 0.51$. *Acetic- α -sulphonepropionic* acid, $\text{COOH}\cdot\text{CHMe}\cdot\text{SO}_2\cdot\text{CH}_2\cdot\text{COOH}$, crystallises in small plates, melting at 129° , and is readily soluble; $K = 1.24$. *$\alpha\beta$ -Sulphonedipropionic* acid, $\text{COOH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{SO}_2\cdot\text{CHMe}\cdot\text{COOH}$, crystallises in spherical aggregates of microscopic needles, is readily soluble, stable in air, and melts at 131° .
J. B. T.

Stereoisomeric Dimethyldihydroxyadipic acids. By NICOLAI D. ZELINSKY and W. ISATIEFF (*Ber.*, 1896, **29**, 819—820).—These acids, $\text{C}_2\text{H}_4[\text{CMe}(\text{OH})\cdot\text{COOH}]_2$, can be obtained in good yield by treating a mixture of acetonylacetone (1 mol.) and potassium cyanide (2 mols.) with strong hydrochloric acid (2 mols.) at 0° , and hydrolysing the product. The acid is added slowly, the mixture left for three days, then treated with an equal volume of strong, hydrochloric acid, and again allowed to remain; the hydrolysis of the dicyanhydrin then takes place at the ordinary temperature. The product was fractionally crystallised from water, and there were obtained (1) a less soluble acid, melting at 212° , with conductivity $K = 0.0317$; and, in small quantity, (2) a more soluble acid, melting at $191\text{--}192^\circ$, and with conductivity $K = 0.0330$, possibly itself a mixture of isomeric acids.
C. F. B.

Two Isomeric Ketodicarboxylic acids. By WILLIAM O. EMERY (*J. pr. Chem.*, 1896, [2], **53**, 303—307).—*Acetonylsuccinic* acid, $\text{COMe}\cdot\text{CH}_2\cdot\text{CH}(\text{COOH})\cdot\text{CH}_2\cdot\text{COOH}$, is prepared by heating ethylic α -acetyltricarballylate (*Abstr.*, 1891, 423) with twice its volume of hydrochloric acid (sp. gr. 1.11) in a reflux apparatus until no more carbonic anhydride is evolved, and evaporating the product on the water bath; it crystallises in laminæ, melts at 107° , and dissolves freely in water; the *silver* and *barium* salts were prepared. When the acid is heated at 200° under 12 mm. pressure, the *anhydride* distils over; it crystallises in small, white prisms, melts at 95° , and dissolves easily in chloroform, but only sparingly in carbon bisulphide; hot water converts it into the acid.

β -Acetylglutaric anhydride, $\text{C}_7\text{H}_8\text{O}_4$, is the product of treating ethylic β -acetyltricarballylate with hydrochloric acid in the manner described

above; it crystallises in prisms, and melts at 102° . The author has not succeeded in converting the anhydride into the acid, but the *silver* and *barium* β -acetylglutarates have been prepared.

A. G. B.

Action of Ethylic β -Bromolevulinate on Ethylic Sodiomalonate. By WILLIAM O. EMERY (*J. pr. Chem.*, 1896, [2], 53, 308—312).—Conrad and Guthzeit (*Abstr.*, 1885, 42; 1886, 336) prepared the ethylic salt of an acid, which they termed α -carboxy- β -acetylglutaric acid, by the action of ethylic β -bromolevulinate on ethylic sodiomalonate; by heating this acid, they obtained one which melted at 109° , and was termed β -acetylglutaric acid. The author finds that the last-named acid really melts at 107° , and is acetonylsuccinic acid (preceding abstract), the immediate product of the action of ethylic β -bromolevulinate on ethylic sodiomalonate being *ethylic carb-oxyacetonylsuccinate*, $\text{COMe}\cdot\text{CH}_2\cdot\text{CH}(\text{COOEt})\cdot\text{CH}(\text{COOEt})_2$, which boils at $188\text{--}189^{\circ}$ (11 mm.), has a sp. gr. = $1\cdot1320$ at $20^{\circ}/4^{\circ}$, and is also formed by the interaction of ethylic acetylacrylate and ethylic sodiomalonate.

A. G. B.

Action of Thiosinamine [Allylthiocarbamide] on Mercuric Iodide in presence of Ammonia. By OTTO FOERSTER (*Chem. Zeit.*, 1895, 19, 1895).—The author shows that by mixing an ammoniacal solution of allylthiocarbamide or of allylthiocarbimide with a solution of mercuric iodide in potassium iodide, an orange-yellow precipitate is obtained, which turns black slowly when exposed to light, or rapidly when treated with potassium cyanide. The yellow precipitate has the constitution $2\text{HgS}, \text{HgI}_2, \text{NH}_3$, and, when treated with potassium cyanide, leaves a black residue of mercuric sulphide.

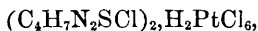
J. J. S.

Thiosinamine [Allylthiocarbamide] III. By J. GADAMER (*Arch. Pharm.*, 1896, 234, 1—47; compare this vol., i, 140).—Allylthiocarbamide dibromide, $\text{C}_4\text{H}_8\text{N}_2\text{SBr}_2$, melts at 139° (Falke gives $136\text{--}137^{\circ}$, Maly $146\text{--}147^{\circ}$); it is not converted into bromopropylene pseudothiocarbamide by recrystallisation. When its aqueous solution is treated with a deficiency of gold chloride, the aurobromide, $\text{C}_4\text{H}_8\text{N}_2\text{SBr}_2, \text{AuBr}_3$ is formed; but an excess of the chloride produces the aurochloride of the bromochloride,



the fact that the second bromine atom remains under this treatment indicates that it is situated differently from the other bromine atom. The *picrate*, $\text{C}_4\text{H}_7\text{N}_2\text{SBr}, \text{C}_6\text{H}_3\text{N}_3\text{O}_7$, melts at $184\text{--}185^{\circ}$. Allylthiocarbamide bromochloride melts at $128\cdot5^{\circ}$. No conclusion was arrived at concerning the nature of the product of the action of silver oxide on the dibromide. The diiodide, $\text{C}_4\text{H}_8\text{N}_2\text{SI}_2$, melts and decomposes at $130\cdot5^{\circ}$; one atom of iodine can be precipitated from it by silver nitrate solution; the *picrate*, $\text{C}_4\text{H}_7\text{N}_2\text{SI}, \text{C}_6\text{H}_3\text{N}_3\text{O}_7$, melts at $178\text{--}179^{\circ}$. The chloriodide, $\text{C}_4\text{H}_7\text{N}_2\text{SI}, \text{HCl}$, was prepared by Maly; it melts at $132\text{--}133^{\circ}$; its *aurochloride* and *platinochloride* were prepared. By the prolonged action of excess of silver nitrate on

the diiodide, and treatment of the filtrate with platinic chloride, a *platinochloride*, $(\text{OH} \cdot \text{C}_4\text{H}_7\text{N}_2\text{S})_2, \text{H}_2\text{PtCl}_6$, was obtained, and an *aurochloride*, $\text{OH} \cdot \text{C}_4\text{H}_7\text{N}_2\text{S}, \text{HAuCl}_4$, was also prepared. Silver oxide converts the diiodide into the *base*, $\text{C}_4\text{H}_7\text{IN}_2\text{S}$. Allylthiocarbamide dichloride was not prepared in a pure condition by the action of chlorine on allylthiocarbamide, but the *platinochloride*,

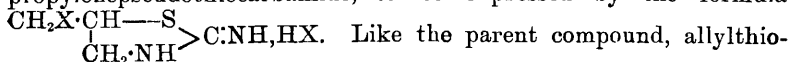


and the *picrate*, $\text{C}_4\text{H}_7\text{N}_2\text{SCl}, \text{C}_6\text{H}_3\text{N}_3\text{O}_7$ (m. p. $173-174^\circ$), are described.

The author has confirmed Gabriel's observations on the conversion of allylthiocarbamide into β -methylethylenepseudothiocarbamide (propylenepseudothiocarbamide) by halogen hydrides, and finds that the change takes place in the cold.

Henry's bromallylthiocarbamide (m. p. 111°) was prepared, and attempts were made to convert it into the isomeric pseudothiocarbamide by Gabriel's method. Since no success attended these efforts, the author concludes that bromallylthiocarbamide is of the form $\text{NH}_2 \cdot \text{CS} \cdot \text{NH} \cdot \text{CH}_2 \cdot \text{CBr} \cdot \text{CH}_3$, not $\text{NH} \cdot \text{CS} \cdot \text{NH} \cdot \text{CH}_2 \cdot \text{CBr} \cdot \text{CH}_3$.

The reduction of allylthiocarbamide bromide and iodide with various reducing agents led to no very definite results, nor did bromine water have the simple oxidising action on the bromide that it has on β -methylethylenepseudothiocarbamide; potassium chlorate and hydrochloric acid, however, oxidised the bromide to β -chlorobromomethyltaurocarbamie acid, a change which resembles the action of bromine water on β -methylethylenepseudothiocarbamide, and, in the author's opinion, warrants the conclusion that the allylthiocarbamide haloids are merely halogen substitution products of Gabriel's propylenepseudothiocarbamide, to be expressed by the formula



Like the parent compound, allylthiocarbamide dibromide combines readily with methylic iodide (compare Beilstein, 1893, [3], i, 1321, 1324).

A. G. B.

Action of Hydrochloric acid on Hydrazodicarbothioallylamide. By MARTIN FREUND and R. L. HEILBRUN (*Ber.*, 1896, **29**, 859-863).—When hydrazodicarbothioallylamide (*Abstr.*, 1894, i, 97) is boiled with hydrochloric acid, three distinct products are obtained. Allyldithiourazole, $\begin{array}{c} \text{NH} \cdot \text{CS} \\ | \\ \text{NH} \cdot \text{CS} \end{array} > \text{N} \cdot \text{C}_3\text{H}_5$, is precipitated from

the acid solution by the addition of water. It is dimorphous, crystallising in long needles and in large rhombohedral crystals, which melt at $136-137^\circ$. The *silver* salt, $\text{C}_6\text{H}_5\text{N}_3\text{S}_2\text{Ag}_2$, is a white, curdy precipitate. When it is treated with methylic iodide, or when the urazole is treated with sodium methoxide, and methylic iodide, *methylallylthiourazole*, $\text{C}_6\text{H}_5\text{MeN}_3\text{S}_2$, is formed; this melts at $68-70^\circ$, and has basic properties, yielding a *hydrochloride* which crystallises in silky needles and melts at $159-161^\circ$. The *diacetyl compound*, $\text{C}_6\text{H}_5\text{Ac}_2\text{N}_3\text{S}_2$, crystallises in yellow plates and melts at 94.5° . The *monacetyl derivative* melts at $176-177^\circ$, and dissolves in sodium carbonate solution. When allyldithiourazole is evaporated with hydrogen

peroxide, a *compound* of the formula. $C_5H_5N_3S_2$, melting at $166-167^\circ$, is produced.

The acid filtrate from the allyldithiourazole contains 1-allyl-5-allylimido-2-thiourazole, which has been previously obtained by Freund and Wischewiansky (Abstr., 1894, 97), and *dipropylene-ψ-hydrazodicarbothiamide*,

$$\begin{array}{c} \text{CHMe}\cdot\text{S} \\ | \\ \text{CH}_2-\text{N} \end{array} \begin{array}{c} \text{S} \\ \text{CH}_2-\text{N} \end{array} \text{NH}\cdot\text{NH}\cdot\text{C} \begin{array}{c} \text{S}\cdot\text{CHMe} \\ | \\ \text{N}\cdot\text{CH}_2 \end{array}$$
 The latter is insoluble in water, forms slender needles, or compact crystals, and melts at $196-197^\circ$. The *hydrochloride* crystallises in needles, melting at 217° , and the *platinochloride* decomposes at about 240° . The *acetyl derivative*, $C_8H_{12}Ac_2N_4S_2$, melts at 242° , whilst the *dimethyl derivative* forms a syrupy mass. When the hydrochloride is treated with sodium nitrite, a *nitroso-compound*, $C_8H_{12}(NO)_2N_4S_2$, is formed which begins to decompose at 110° . A. H.

Water of Crystallisation and Reactions of Alloxantin. By C. HEINRICH L. RITTHAUSEN (*Ber.*, 1896, 29, 892-893).—The formula of alloxantin is stated in some text-books, including Beilstein, to be $C_8H_4N_4O_7 + 3H_2O$, in others to be $C_8H_6N_4O_8 + 2H_2O$; the author has analysed two preparations of different origin and finds that the latter formula is correct. The compound becomes completely anhydrous after heating at 150° during 1-1½ hours, or at $107-110^\circ$ for about five hours. A purple solution is obtained by heating alloxantin (1-2 milligrams) with a drop of nitric acid (sp. gr. = 1.4), constantly stirring until the acid is volatilized, and dissolving the residue in a little ammonia and water. Convicin reacts in a similar manner (compare following Abstr.).

J. B. T.

Alloxantin as a Decomposition Product of Convicin from Sow-beans (*Vicia faba minor*) and Vetches (*Vicia sativa*). By C. HEINRICH L. RITTHAUSEN (*Ber.*, 1896, 29, 894-896).—A compound, apparently identical with convicin from vetch seed, crystallises from alcoholic extract of sow-beans, the yield is 60 grams from 150 kilos. of beans. When boiled for two minutes with dilute sulphuric acid (1:2), it slowly deposits alloxantin. The same result is obtained by dissolving convicin in concentrated hydrochloric acid, the yield being about 36 per cent of the convicin employed. Convicin from vetch seed acts in a similar manner, its formula is $C_{10}H_{15}N_3O_7 + H_2O$, not $C_{10}H_{14}N_3O_7 + H_2O$, as previously stated; although identical with the compound from sow-beans in appearance and behaviour with acids, the latter appears to have the formula $C_{10}H_{16}N_3O_8\cdot H_2O$. The alloxantin was identified by analysis, and by its various colour reactions. J. B. T.

Deoxyfuroïn. By RICHARD BADER (*Chem. Zeit.*, 1895, 19, 1939).—Furoïn (Fischer, Abstr., 1882, 499), when reduced in alcoholic solution by means of tin foil and concentrated hydrochloric acid yields *deoxyfuroïn*. The reaction is carried out in the cold and is complete when a portion of the solution no longer gives a dark

green colour if treated with caustic soda. The solution is filtered, gradually diluted with water, and extracted several times with ether; the combined ethereal extract is then washed 10—12 times with cold water and dried over calcium chloride, and the brownish syrup which is left on evaporating the ether is purified by distillation in steam. *Deoxyfuroïn* distils between 250° and 260° under a pressure of 755 mm., at the same time undergoing slight decomposition. The distillate on cooling sets to a mass of large, thick crystals which melt again at the ordinary temperature, and undergo decomposition when exposed to the air and bright sunlight. It is readily soluble in most organic solvents, slightly in hot water and readily in cold sodium hydroxide solution. No oxime or hydrazone could be obtained.

Benzofuroïn, when reduced in a similar manner, yields *deoxybenzofuroïn* in small quantities.
J. J. S.

Furfuraldehyde and Carbonic Anhydride from Glycuronic acid. By F. MANN and BERNHARD TOLLENS (*Annalen*, 1896, **290**, 155—158).—Glycuronic acid is prepared from Purree, or Indian yellow, by digesting it with dilute hydrochloric acid, submitting it to pressure, and hydrolysing with 10 per cent. sulphuric acid the euxanthic acid extracted from the residue; the specific rotatory power of glycuronic anhydride is $[\alpha]_D = +18.2^{\circ}$.

It having been shown that glycuronic anhydride yields furfuraldehyde on distillation with hydrochloric acid (Abstr., 1892, 1433), the authors have attempted to express the action quantitatively; from 1 gram of the anhydride, 15 per cent. of furfuraldehyde, and 26.5 per cent. of carbonic anhydride have been obtained, the equation $C_6H_8O_6 = C_5H_4O_2 + 2H_2O + CO_2$ requiring 54 per cent. and 25 per cent. respectively.

Furfuraldehyde has been also obtained from euxanthic, urochloralic, and urobutylechloralic acids.
M. O. F.

Preparation of Siliconchloroform, Siliconbromoform, and Triphenylsiliconprotane. By CHARLES COMBES (*Compt. rend.*, 1896, **122**, 531—533).—On passing dry hydrogen chloride over copper silicide, heated in a vapour bath of either sulphur, mercury, or diphenylamine, siliconchloroform is produced in quantities of about 80 per cent. of the theoretical yield, the remaining 20 per cent. consisting chiefly of the tetrachloride, from which it can be readily separated by fractionation.

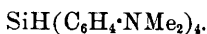
With hydrogen bromide, a somewhat smaller quantity of the corresponding bromo-derivative is produced, owing to partial dissociation of the halogen acid, with formation of copper bromide.

With hydrogen iodide, no siliconiodoform is produced.

On mixing dry ethereal solutions of aniline and siliconchloroform, a crystalline substance, $SiHCl(NHPh)_2$, separates on concentration; when excess of aniline is employed, the compound $SiH(NHPh)_3$ is produced. The latter, when treated with dry hydrogen chloride, is converted into aniline hydrochloride and siliconchloroform thus

showing that nitrogen intervenes between the silicon and the phenyl group. J. F. T.

Derivatives of Triphenylsiliconprotane. By CHARLES COMBES (*Compt. rend.*, 1896, **122**, 622—624; compare preceding abstract).—By the action of sodium on a dry ethereal solution of molecular proportions of silicon tetrachloride and parabromodimethylaniline a voluminous crystalline mass is produced of the formula



This, on recrystallisation from hot light petroleum, forms slender, needle-shaped crystals, melting and decomposing at 225°.

By operating in the same way with siliconchloroform, the compound $\text{SiH}(\text{C}_6\text{H}_4\cdot\text{NMe}_2)_3$ is produced; it crystallises from acetone in small prisms, and melts at 152°.

On oxidation, these substances readily produce colouring matters. They are, however, the same as those produced by the oxidation of dimethylaniline, and do not contain silicon.

$\text{OH}\cdot\text{Si}(\text{C}_6\text{H}_4\cdot\text{NMe}_2)_3$ is produced by the action of mercuric nitrate on the triphenyl derivative, it melts at 183—189°, and is soluble in all the usual solvents. J. F. T.

Formation of 1 : 2 : 3-Trimethylbenzene together with Synthetical Mesitylene. By AD. LUCAS (*Ber.*, 1896, **29**, 953—958; compare Abstr., 1895, i, 356).—Acetone purified by means of sodium hydrogen sulphite is converted by the action of sulphuric acid, into mesitylene, which is purified by repeated fractionation over sodium; the portion boiling at 160—170° yields with acetic chloride, mesityl methyl ketone, and this, when oxidised, gives mesityl glyoxalic acid, $\text{C}_6\text{H}_3\text{Me}_3\cdot\text{CO}\cdot\text{COOH}$, which is then distilled. Unchanged mesityl glyoxalic acid is removed from the distillate by treating it with water at 30° (Claus' statement as to its insolubility being incorrect), and the remaining acid is then etherified by V. Meyer's method; in this manner, the three trimethylbenzoic acids, 1 : 2 : 4 : 6-, 1 : 2 : 3 : 4-, and 1 : 3 : 4 : 5-, [$\text{COOH} = 1$], are formed, the last in smallest quantity. No isomeric acid derived from 1 : 2 : 4-trimethylbenzene (pseudocumene) could be detected. The trimethylbenzaldehyde, which is also formed by the distillation of the glyoxalic acid, yields, in addition to mesityl antialdoxime (m. p. 124—125°), a synaldoxime melting at 168°, and an antialdoxime which crystallises in lustrous prisms melting at 115°; both are probably derived from the aldehyde [$\text{CHO} : \text{Me}_3 = 1 : 2 : 3 : 4$]. No 1 : 2 : 4-trimethylbenzene derivatives could be detected. About 10 per cent. of the original trimethylbenzene consisted of the 1 : 2 : 3-compound, and the remainder of mesitylene. The higher fractions obtained in the original distillation after the separation of the trimethylbenzenes, are readily oxidised by potassium permanganate, and do not consist of benzene derivatives. Attempts were made to prepare trimethylbenzene by passing methylacetylene through heated tubes containing pumice; in spite of varying the

temperature, only carbonaceous matter could be obtained; under similar circumstances, acetylene yields comparatively little benzene, but more highly condensed compounds, carbonaceous matter also is produced in considerable quantity (compare following abstract).

J. B. T.

Synthesis and Constitution of Benzene. By ARTHUR R. HANTZSCH (*Ber.*, 1896, **29**, 958—960).—The direct condensation of acetone to trimethylbenzene can only yield the symmetrical compound, but if, as Fittig has suggested, methylacetylene is first formed, and the group CH combines with only one additional carbon atom (peripheral linkage) the trimethyl compounds 1 : 3 : 5- and 1 : 3 : 4- should be produced. The investigations of Lucas (preceding abstract) show that the latter compound is not formed at all, the condensation products being only 1 : 3 : 5- and 1 : 2 : 3-, the latter in smaller proportion. This suggests that each carbon atom actually combines with two others (centric linkage), which fully accords with the facts. A combined peripheral and centric linkage should give rise to all three trimethylbenzenes, and, therefore, need not be considered. Von Baeyer's observations on the stability of the para-linkage in reduced benzene derivatives thus receive support from a synthetical standpoint.

J. B. T.

Formation of Salts from Trinitrobenzene. By VICTOR MEYER (*Ber.*, 1896, **29**, 848—850).—The author considers that the coloured solutions which polynitro-compounds give with alkalis contain salts formed by the replacement of hydrogen in the benzene nucleus. Lobry de Bruyn, on the other hand, supports the view that the formation of these coloured solutions is accompanied by a decomposition which results in the formation of nitrous acid. When pure trinitrobenzene, however, is treated with pure soda, which produces a red coloration, and pure sulphuric acid is immediately added, no nitrons acid can be detected in the liquid. Precisely similar results are obtained with pure trinitrobenzoic acid. Dinitrothiophen, moreover, yields a reddish-brown silver salt which is decomposed by hydrochloric acid with regeneration of the pure dinitro-compound. Lobry de Bruyn's salt, $C_6H_3(NO_2)_3 + KOCH_3 + \frac{1}{2}H_2O$, probably has the constitution $C_6H_2K(NO_2)_3 + CH_3 \cdot OH + \frac{1}{2}H_2O$.

A. H.

New Synthesis of some Aromatic Nitriles. By ALEXANDRE DESGREZ (*Bull. Soc. Chim.*, 1895, [3], **13**, 735—737).—Under suitable conditions, cyanogen may be made to act as a halogen, and directly displace hydrogen in such hydrocarbons as benzene, toluene, the two xylenes, and mesitylene; the yield is about 12 per cent. of the theoretical.

The method employed is to conduct the cyanogen gas into the hydrocarbon (boiling under a slight pressure) in the presence of aluminium chloride. By this means, the author has synthesised benzonitrile, which he has characterised by the formation of ethylic benzoate, benzamide, and benzoic acid.

In the formation of cyanogen from mercuric cyanide, the action

2 h 2

is sensibly accelerated by the presence of a small quantity of mercuric chloride. J. F. T.

Mandelonitrile. By ERNST S. C. VON MEYER (*J. pr. Chem.*, 1896, [2], 53, 344).—With the intention of preparing amidobenzyl cyanide, mandelonitrile was left in contact with the calculated proportion of alcoholic ammonia, and gradually evaporated; small crystals of the formula, $C_{15}H_{12}N_2$, were obtained. The substance is being investigated, and this publication is made in view of E. Fischer's paper on the formation of oxazoles (this vol., i, 262). A. G. B.

Distillation of Orthocresol with Lead Oxide. By BERTHOLD JEITELES (*Monatsh.*, 1896, 17, 57—64).—Orthocresol, with about twice its weight of lead oxide, is heated for some time in a reflux apparatus, and then distilled; the distillate, when shaken with strong caustic potash, leaves undissolved a reddish *substance*, which is crystallised from alcohol, thereby becoming pale yellow. On sublimation, it condenses in long, white needles which begin to sublime at 150° and melt at 162 — 163° . When treated with sulphuric acid, the substance gives the greenish-blue fluorescence characteristic of xanthenes. On reduction with hydriodic acid, it yields a *substance* which is volatile in steam, crystallises from alcohol in white scales, melts at 93° , and gives the xanthone reaction with sulphuric acid. This compound is attacked by alcoholic potash, yielding a phenolic *substance* which dissolves readily in alcohol, and, with phenylhydrazine, gives an ill-defined *compound* containing nitrogen. When fused with potash, it is decomposed with production of a phenol which gives a slight precipitate with bromine water, and an acid, volatile in steam, which crystallises in white needles, and shows the salicylic acid reaction with ferric chloride.

The author is of opinion, although the evidence is inconclusive, that he was probably dealing with a monomethylxanthone. A. L.

Dibromopseudocumenol Bromide and analogous Compounds. By KARL AUWERS (*Ber.*, 1896, 29, 1095—1110; compare this vol., i, 149).—It has been already shown that bases act on dibromopseudocumenol bromide with great readiness, and its behaviour towards aniline, piperidine, dimethylaniline, and pyridine has been studied (*loc. cit.*).

Ammonia gives rise to two products, $C_9H_9Br_2O \cdot NH_3$, and $(C_9H_9Br_2O)_3N$, according to the experimental conditions, whilst the action of aliphatic monamines leads to the formation of tertiary ammonium compounds. Although quinoline and tertiary bases generally yield additive compounds, aqueous trimethylamine is without action, and the solution in benzene loses hydrogen bromide, yielding a compound which does not dissolve in alkalis, and is probably identical with the substance obtained by decomposing the pyridine derivative, or by allowing the original bromide to remain in contact with aqueous soda.

The active bromine atom of dibromopseudocumenol bromide has

been replaced by chlorine and iodine, and the compounds thus produced closely resemble the original bromide; the acetate of dibromohydroxypseudocumenol (this vol., i, 151), which melts at 113°, forms the intermediate compound in the production of these substances, and from this circumstance is drawn the conclusion that the bromide, chloride, iodide, and acetate are analogous in structure, and, as the constitution of the last-named is most plausibly represented by the formula $\text{CO} < \begin{smallmatrix} \text{CMe}:\text{CBr} \\ \text{CBr}:\text{CMe} \end{smallmatrix} > \text{CMe}\cdot\text{OAc}$, it follows that Zincke's interpretation of the structure of dibromopseudocumenol bromide (this vol., i, 214) is correct. The experimental matter on which this deduction depends is dealt with in the following abstracts.

The author has already described a remarkable nitro-compound obtained by the action of fuming nitric acid on pseudocumenol (Abstr., 1885, 380) having the formula $\text{C}_9\text{H}_{10}\text{N}_2\text{O}_5$; it melts at 81·5° (not at 84°), and, although insoluble in alkali, is readily converted by alcoholic ammonia into the true dinitropseudocumenol, with which it is isomeric, and easily loses a nitro-group, passing into nitropseudocumenol. Whilst recent investigation has shown that the last-named is orthonitropseudocumenol, and not the meta-compound, the position of the second nitro-group has not been determined. Owing to the readiness with which yellow ammonium sulphide eliminates the nitro-group, the compound in question forms a convenient source of orthonitropseudocumenol, which cannot be obtained by direct nitration of the phenol.

An analogous *nitro-compound* of dibromopseudocumenol is obtained by the action of cold, fuming nitric acid; it has the formula $\text{C}_9\text{H}_5\text{Br}_2\text{NO}_3$, melts at 102—103°, and crystallises from a mixture of ether and petroleum in splendid plates. The isomeric *dibromopseudocumenol nitrite* is obtained by the action of silver nitrite on dibromopseudocumenol bromide dissolved in benzene; it crystallises from petroleum in yellowish, lustrous plates, and melts, evolving gas, at 135°. It is probable that this compound has the constitution $\text{CO} < \begin{smallmatrix} \text{CMe}:\text{CBr} \\ \text{CBr}:\text{CMe} \end{smallmatrix} > \text{CMe}\cdot\text{NO}_2$, as hot dilute alkali converts it into the stilbene derivative obtained under similar conditions from dibromopseudocumenol bromide, nitrous acid being eliminated.

When pseudocumenol is chlorinated by Reimer's method, a product is obtained which melts at 96·5° (not at 98°), and has the empirical formula $\text{C}_{10}\text{H}_{12}\text{Cl}_2\text{O}$. It is indifferent towards aniline, phenylhydrazine, and phenylic cyanate, and undergoes no change when heated with a mixture of fuming nitric and concentrated sulphuric acids. According to the experimental conditions, bromine gives rise to two compounds, $\text{C}_{10}\text{H}_{10}\text{Cl}_2\text{Br}_2\text{O}$, which crystallises from glacial acetic acid in long needles, and melts at 147°, and $\text{C}_{10}\text{H}_5\text{Cl}_2\text{Br}_3\text{O}$, which is obtained in lustrous leaflets, and melts at 203—204°. M. O. F.

Dibromopseudocumenol Bromide, Chloride, and Iodide. By KARL AUWERS and L. HOF (*Ber.*, 1896, 29, 1110—1120; compare the foregoing abstract).—When dibromopseudocumenol bromide in benzene solution is agitated with concentrated aqueous ammonia, the

compound $N(\text{CH}_2\cdot\text{C}_6\text{Me}_2\text{Br}_2\cdot\text{OH})_3$ is produced; it crystallises from xylene in short needles, and melts between 218° and 224° , according to the rate at which the temperature rises. The substance dissolves readily in ether, being more sparingly soluble in alcohol and benzene, and almost insoluble in chloroform and petroleum; it is indifferent towards hot alkalis, and is converted by glacial acetic acid into tetrabromodihydroxytetramethylstilbene (this vol., i, 150). The *hydrobromide* melts and decomposes at 236° ; the *ethyl ether* crystallises from glacial acetic acid in lustrous prisms, and melts at $196\text{--}197^\circ$.

If gaseous ammonia is passed into a benzene solution of dibromopseudocumenol bromide during several hours, the filtered liquid deposits the compound $\text{NH}_2\cdot\text{CH}_2\cdot\text{C}_6\text{Me}_2\text{Br}_2\cdot\text{OH}$, which separates from a mixture of chloroform and petroleum in white, prismatic crystals, and melts at 106° ; it dissolves readily in ether, chloroform, and benzene; with difficulty, however, in petroleum. The *hydrobromide* crystallises from glacial acetic acid in needles, and melts at $159\text{--}161^\circ$, the solvent converting it into the stilbene compound already mentioned. On adding water to the solution of the amine in acetic acid, the acetate of dibromopseudocumenol, which melts at 115° , is produced.

When aqueous methylamine is added to dibromopseudocumenol bromide dissolved in benzene, the *methylamine derivative*,

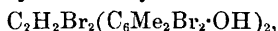


is produced; it crystallises from chloroform in needles, and melts at 173° when rapidly heated. It undergoes no change when heated alone on the water bath, but boiling caustic soda converts it into the stilbene derivative. The *hydrobromide* crystallises from chloroform, and melts at 195° ; the *phenylurethane derivative* crystallises from a mixture of chloroform and petroleum in white prisms, and melts at 202° .

The *ethylamine derivative* of dibromopseudocumenol bromide, $\text{NEt}(\text{CH}_2\cdot\text{C}_6\text{Me}_2\text{Br}_2\cdot\text{OH})_2$, crystallises from chloroform and petroleum in rhombic prisms, and melts at 165.5° ; the *hydrobromide* separates from glacial acetic acid in needles, sinters at 130° , and melts, decomposing, at 218° . The *diethylamine derivative* of dibromopseudocumenol bromide, $\text{NEt}_2\cdot\text{CH}_2\cdot\text{C}_6\text{Me}_2\text{Br}_2\cdot\text{OH}$, melts at 87° ; the *hydrobromide* crystallises from chloroform in needles, and melts at 182° .

As already stated (foregoing abstract), aqueous trimethylamine is without action on dibromopseudocumenol bromide; the solution in benzene, however, eliminates hydrogen bromide, and converts it into the compound $\text{C}_{18}\text{H}_{16}\text{Br}_4\text{O}_2$, which is insoluble in alkalis, crystallising from aniline, naphthalene, and nitrobenzene in dark brown needles which melt at 230° , and evolve gas at 250° . The same product is formed under the influence of 10 per cent. aqueous caustic soda, the stilbene derivative also being formed. Moist silver oxide, however, converts dibromopseudocumenol bromide into an amorphous compound, $\text{C}_9\text{H}_{10}\text{Br}_2\text{O}_2$, which melts at $240\text{--}245^\circ$.

Tetrabromodihydroxytetramethylstilbene bromide,



is obtained by adding bromine to the stilbene derivative already

mentioned; it crystallises from glacial acetic acid and petroleum, and melts at 179°.

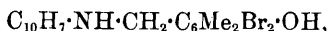
Dibromopseudocumenol iodide, $C_6Me_3Br_2 \cdot OI$, is obtained by the action of hydriodic acid on the acetate of dibromopseudocumenol, and crystallises from glacial acetic acid in white needles which melt at 134—136°; it closely resembles the bromide in properties, and is converted by boiling methylic alcohol into dibromomethoxyypseudocumenol.

Dibromopseudocumenol chloride, $C_6Me_3Br_2 \cdot OCl$, is produced when hydrogen chloride acts on the acetate, and crystallises from glacial acetic acid or petroleum in needles melting at 109—110°.

During the preparation of dibromopseudocumenol bromide, in addition to the stilbene derivative, there are formed two bye-products, the compound $C_{11}H_{13}Br_2O$, which crystallises in white needles and melts at 174°, and the compound $C_9H_9Br_3O$, isomeric with dibromopseudocumenol bromide, which crystallises from glacial acetic acid in white needles and melts at 181°.

M. O. F.

Products obtained from Dibromopseudocumenol Bromide by the Action of Aromatic Bases. By KARL AUWERS and H. A. SENTER (*Ber.*, 1896, 29, 1120—1128; compare the foregoing abstracts).—The *β*-naphthylamine derivative,



is obtained by the action of *β*-naphthylamine on dibromopseudocumenol bromide dissolved in benzene, the stilbene derivative being formed at the same time; it crystallises from benzene in silvery leaflets, and melts at 181—182°. The substance is insoluble in water, ether, and petroleum, and is decomposed by hot glacial acetic acid, yielding the stilbene derivative; dilute soda is without action on the compound, and dissolves it slowly.

The *methylaniline derivative*, $OH \cdot C_6Me_2Br_2 \cdot CH_2 \cdot NMePh$, is prepared by adding dilute hydrochloric acid to a mixture of dibromopseudocumenol bromide and methylaniline, the *hydrochloride* thus obtained being then decomposed with soda; it crystallises from alcohol and petroleum in small, white needles, and melts at 99°. The *hydrobromide* loses hydrogen bromide at 60°.

The *quinoline additive-compound*, $C_9H_9Br_3O \cdot C_8H_7N$, is insoluble in benzene, xylene, petroleum, acetone, and ethylic acetate, but crystallises from glacial acetic acid containing hydrogen bromide, and melts at 226°; if water is added to the solvent, dibromopseudocumenol acetate is produced.

The *diethylaniline derivative*, $OH \cdot C_6Me_2Br_2 \cdot CH \cdot NEt_2Ph$, crystallises from alcohol in long, slender needles, and melts at 89—90°; it is obtained by the action of boiling 10 per cent. soda on the *diethylaniline additive-compound*, which crystallises from glacial acetic acid in long, transparent needles melting at 256—257°.

The *methiodide* of the dimethylaniline derivative (this vol., i, 150) is obtained by heating the substance in benzene solution with methylic iodide at 100°; it crystallises in yellowish, lustrous leaflets, and melts and decomposes at 190—191°. The *ethobromide* crystallises

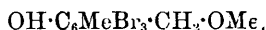
in slender, pale brown needles, which melt and evolve gas at $189\text{--}192^\circ$; caustic soda converts it into a crystalline substance which melts at $153\text{--}154^\circ$. When the methiodide is treated with dilute aqueous soda, hydrogen iodide is eliminated, and the base $\text{C}_{18}\text{H}_{23}\text{Br}_2\text{NO}_2$ is produced, being also formed by the action of moist silver oxide on the methiodide; it is strongly alkaline towards litmus, and when crystallised from water melts at $205\text{--}207^\circ$.

The *methiodide* of the diethylaniline derivative melts at $177\text{--}178^\circ$, and is converted by soda into a *base*, which crystallises from hot water in lustrous needles, and melts at $191\text{--}192^\circ$.

The *hydriodide* of the aniline derivative is obtained by heating it with methylic iodide in benzene solution; it crystallises in needles, and melts at 182° . The *hydriodide* of the piperidine compound is prepared in the same manner, and crystallises in short prisms, melting at 206° .
M. O. F.

Bromo-derivatives of Asymmetrical Metaxylenol. By KARL AUWERS and G. VON CAMPENHAUSEN (*Ber.*, 1896, **29**, 1129—1132; compare the foregoing abstracts).—When bromine acts on asymmetrical metaxylenol during a short period, Jacobsen's tribromoxylenol (m. p. 179°) is the sole product; if the action, however, is protracted, the main product consists of tribromoxylenol bromide, along with the dibromide, which does not dissolve in petroleum.

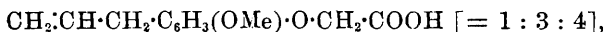
Tribromoxylenol bromide, $\text{C}_6\text{Me}_2\text{Br}_3\cdot\text{OBr}$, crystallises from petroleum in long, lustrous needles, and melts at $135\text{--}136^\circ$; boiling methylic alcohol converts it into *tribromomethoxyxylenol*,



which crystallises from petroleum in slender, white needles, and melts at 100° . *Tribromomethoxyxylenol* melts at $110\text{--}112^\circ$.

Tribromoxylenol dibromide, $\text{OH}\cdot\text{C}_6\text{Me}_2\text{Br}_3\cdot\text{Br}_2$, crystallises from glacial acetic acid in lustrous, white needles, and melts at $169\text{--}171^\circ$; boiling methylic alcohol converts it into *tribromodimethoxyxylenol*, which crystallises from petroleum in slender needles, and melts at $93\text{--}95^\circ$. *Tribromodiethoxyxylenol* melts at $62\text{--}64^\circ$.
M. O. F.

Derivatives of Eugenol. By CH. GASSMANN (*Compt. rend.*, 1896, **122**, 395—397).—*Eugenolacetic acid*,



is obtained by boiling eugenol with sodium hydroxide and chloracetic acid, precipitating with hydrochloric acid, and recrystallising from water at 70° . It melts at 75° , and dissolves in hot water, and most organic solvents. The salts are not decomposed by carbonic anhydride, and the sodium salt is precipitated from its aqueous solution by sodium chloride.

Isoeugenolacetic acid, $\text{CHMe}\cdot\text{CH}\cdot\text{C}_6\text{H}_3(\text{OMe})\cdot\text{O}\cdot\text{CH}_2\cdot\text{COOH}$, is obtained by boiling eugenolacetic acid with a solution of potassium hydroxide. It is essential to a good yield that precipitation with hydrochloric acid should take place between 0° and 5° . Another method is to heat eugenolacetic acid with 2.5 times its weight of potassium

hydroxide and five times its weight of water at 150° for 10 hours, or at 200° for half an hour, and a third method is to heat isoeugenol with sodium hydroxide and chloracetic acid. Isoeugenolacetic acid crystallises in white needles, which melt at 92—94°, and dissolve in most organic solvents. Its salts are less soluble than those of eugenolacetic acid, and are precipitated from their aqueous solutions by sodium hydroxide.

Vanillinacetic acid, $\text{CHO} \cdot \text{C}_6\text{H}_3(\text{OMe}) \cdot \text{O} \cdot \text{CH}_2 \cdot \text{COOH}$ [= 1 : 3 : 4], is obtained by oxidising an alkali salt of isoeugenolacetic acid with potassium permanganate in presence of acetic or carbonic acid. It crystallises from alcohol in colourless crystals which melt at 188—190°, and is identical with the acid obtained from vanillin by the action of chloracetic acid in presence of an alkali. When treated with phosphorus pentachloride, it yields vanillin. C. H. B.

Derivatives of Cholesterol. By JULIUS MAUTHNER and WILHELM SUIDA (*Monatsh.*, 1896, 17, 29—49; compare *Abstr.*, 1894, i, 326, 486).—Of the three cholesterylenes described by Zwenger, and assigned by him the formula $\text{C}_{27}\text{H}_{42}$, *a*-cholesterylene has a molecular weight in naphthalene considerably greater than that corresponding with the above formula, whilst *b*-cholesterylene under the same conditions gives numbers agreeing with a molecular weight twice as great as that assigned to it by its discoverer. *a*-Cholesterylene, contrary to Zwenger's statements, does not melt at 240°, but sinters and turns yellow at 210—220°, becomes transparent at 235°, and liquefies finally at about 260°.

a-Cholesterone and *b*-cholesterone melted, not at 68° and 175°, but at 79·5—80·5° and 192° respectively. The latter compound is identical in properties with Walitzky's cholesterylene (compare this Journal, 1877, i, 58), and may be advantageously prepared in the following manner. Equal weights of anhydrous cholesterol and copper sulphate are mixed and heated at 200°; when cool, the product is extracted with benzene, the filtered solution evaporated, and the residue heated with alcohol; cholesterylic ether is left undissolved, whilst the cholesterylene dissolves and separates on cooling in large needles, whose geometrical and optical properties point to monosymmetric or orthorhombic symmetry respectively; in the former case, the geometrical constants are $a : b : c = 1.1341 : 1 : ?$, $\beta = 131^\circ 59' 40''$, and in the latter, $a : b : c = 0.8359 : 1 : 0.7525$. The substance is oxidised very slowly by alkaline permanganate, although its behaviour towards bromine and iodine demonstrates the presence of one ethylic union in the molecule. The *cholesterylic ether*, $(\text{C}_{27}\text{H}_{43})_2\text{O}$, is also formed on heating a mixture of cholesterylic chloride and zinc dust or zinc oxide at 200°, and appears as a bye-product in the preparation of cholesterylic chloride; it crystallises from a mixture of benzene and alcohol in attenuated, felted needles, sinters at 188°, and melts at about 195°; it is insoluble in alcohol, dissolves sparingly in ether, and readily in benzene and chloroform, its molecular weight in the last substance being normal; the crystals break up in sulphuric acid without producing fluorescence, the liquid on being warmed assuming a reddish-orange colour. By the action of bromine, the substance yields a

tetrabromide, $(C_{27}H_{43}Br_2)_2O$, which crystallises in slender needles, and melts with disengagement of gas at $164-166^\circ$.

Cholesterylic chloride, when heated above its melting point, evolves hydrogen chloride, and at 150° a colourless, limpid liquid passes over; whilst at $345-390^\circ$ a yellow oil with a violet fluorescence distils, leaving a deep brown, gummy residue. The portion of low boiling point redistils for the most part at $110-130^\circ$; its molecular weight combined with its behaviour towards bromine prove it to be a mixture of a paraffin and an olefine, probably octane and octylene. The portion of higher boiling point shows the cholesterol and cholestol reactions, combines with bromine, and has the composition $C_{19}H_{28}$.

Walitzky's cholesterylene, on distillation, yields a mixture of liquids which boil at $240-270^\circ$, $360-390^\circ$, and $400-410^\circ$; the last two probably have the formulæ $C_{16}H_{24}$ and $C_{20}H_{30}$ respectively.

By the action of silver nitrate on cholesterylic chloride in alcoholic solution, a *substance* of uncertain composition is obtained. It contains nitrogen, but no chlorine, crystallises from ethylic or methylic alcohol in beautiful, long crystals, melts at $81-82^\circ$, and, during solidification, the fused substance shows a magnificent play of colours. If in the preparation of this substance the solution be kept neutral by means of carbonic anhydride, no crystals are obtained, but if the product be extracted with ether, the solution evaporated, and the residual oil heated with nitric acid, the above substance crystallises out.


Nitrocholesterylic chloride has the normal molecular weight in naphthalene.

The authors mention that by the oxidation of cholesterol they have obtained a semi-crystalline substance, which yields a ketone whose hydrazone crystallises in beautiful golden-yellow needles. A. L.

Veratrylamine. By CHARLES MOUREU (*Compt. rend.*, 1896, **122**, 477-479).—*Veratrylamine*, $NH_2 \cdot C_6H_3(OMe)_2$ [= 1 : 3 : 4], is obtained by the reduction of nitroveratrol, $NO_2 \cdot C_6H_3(OMe)_2$. It crystallises from ether in brilliant, pale grey plates with a violet tinge, melts at $85-86^\circ$, and boils at $174-176^\circ$ under a pressure of 22 mm. When freshly distilled, it is quite white, but gradually alters and becomes darker in colour when exposed to the air. The platino-chloride melts and decomposes at 220° . *Benzoveratrylamine* forms slender, white needles which melt at 177° .

When diazotised in presence of hydrobromic acid and finely divided copper, veratrylamine yields *bromoveratrol*, an oily liquid, which boils at $250-254^\circ$, but distils easily with water. When diazotised in presence of cuprous cyanide, it yields a cyano-derivative which is identical with the nitrile obtained by Garelli's reaction, and yields veratric acid when hydrolysed. It follows that in veratrylamine $[NH_2 : OMe : OMe = 1 : 3 : 4]$. C. H. B.

Sulphur Nitride. By RUDOLF SCHENCK (*Annalen*, 1896, **290**, 171-185). The author discusses the properties of sulphur nitride,

N_4S_4 , and regards it as having the constitution .

Sulphur nitride is obtained by passing dry ammonia gas into a solution of sulphur dichloride in benzene; it crystallises from carbon bisulphide in orange needles, melting at 178° , and not at 160° , as stated by previous investigators. The highly explosive character of the substance renders it advisable to preserve it in cardboard boxes instead of glass bottles. On adding it to a solution of sodium ethoxide (4 mols.) in alcohol, the liquid acquires a colour which is purple-red by transmitted, and dark green by reflected light, gradually becoming violet and ultimately brown; this coloration is permanent in absence of water, but if water is added the solution becomes yellow and acquires a most offensive odour. Absolute ether precipitates from the alcoholic solution a substance which crystallises in lustrous scales, and exhibits dichroism; it is excessively unstable, and the solution in alcohol is red.

Sulphur nitride is indifferent towards primary and secondary bases of the aromatic series and all tertiary bases. If the substance is covered with piperidine, heat is generated, ammonia and nitrogen being evolved, whilst the mass, on cooling, deposits thiopiperidine (Abstr., 1895, i, 430); the action proceeds quantitatively in accordance with the equation $3\text{N}_4\text{S}_4 + 24\text{C}_5\text{H}_{10}\text{NH} = 12(\text{C}_5\text{H}_{10}\text{N})_2\text{S} + 8\text{NH}_3 + 2\text{N}_2$.

When sulphur nitride is heated for one hour with dimethylamine, and the product distilled, the fraction which boils below 100° is a colourless oil, which solidifies in a mixture of ice and salt; this substance is thiodimethylamine, crystallising in lustrous leaflets having a disagreeable, irritating odour. Ethylamine acts on sulphur nitride, producing tetrethylthiodiamine, $\text{S}(\text{NEt}_2)_2$ (Abstr., 1895, i, 264).

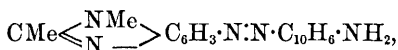
Sulphur nitride converts benzylamine into polymerised benzonitrile, the cyaphenine of Pinner and Klein (*Ber.*, **11**, 6), ammonia and nitrogen being evolved; when, however, the generation of heat is checked, and excess of benzylamine is employed, the *thionamide* of thiobenzoic acid, $\text{S}:\text{CPh}:\text{N}:\text{S}$, is produced, crystallising from ethylic acetate in beautiful yellow prisms, melting at $104\text{--}105^{\circ}$. Along with this, a liquid is formed which becomes deep red when exposed for some days to air; on acidification, ether extracts the colouring matter, which consists of dithiobenzoic acid.

Cold phenylhydrazine is without action on sulphur nitride, but on application of heat, there is a violent disengagement of ammonia and nitrogen, benzene, sulphur, and hydrogen sulphide being also produced.

M. O. F.

Derivatives of α -Diamidodimethylaniline. By A. SCHUSTER and JOHANNES PINNOW (*Ber.*, 1896, **29**, 1053—1057; compare Abstr., 1894, i, 281).— β -Dinitrodimethylaniline is best prepared by the action of 30 per cent. nitric acid on dimethylaniline dissolved in dilute sulphuric acid, and yields diamidodimethylaniline on reduction. When the base is boiled with acetic anhydride, methylethenylacetamidophenylenamidine is formed, along with diacetdiamidodimethylaniline, which melts at $151.5\text{--}152.5^{\circ}$ (uncorr.), and crystallises from water with $1\frac{1}{2}\text{H}_2\text{O}$ (compare Wurster and Sendtner, *Ber.*, **12**, 1806). Methylethenylamidophenylenamidine melts at

167—168° (uncorr., compare Abstr., 1894, i, 281). The *picrate* melts at 248° (uncorr.). The solution of the corresponding diazo-compound can be boiled without undergoing decomposition. With β -naphthylamine, the diazo-salt yields a *colouring matter*,



which crystallises from aniline in orange-coloured needles, and melts and decomposes at 260° (uncorr.). This colouring matter is taken up by unmordanted cotton.

Methylethylnitroacetamidophenylenamidine is formed by the nitration of the acetyl compound in presence of concentrated sulphuric acid. It crystallises from acetic acid in compact needles containing 1 mol. of the solvent, and melts, after drying, at 220—221° (uncorr.).

Methylethylnitramidophenylenamidine crystallises in red needles, melting at 251—252° (uncorr.). When reduced, it yields *methyl-diethylnitramidobenzene*, which crystallises from water in needles; these contain 1H₂O, and, after drying, do not melt below 260°. The *double salt* of the hydrochloride of this base with mercuric chloride forms lanceolate needles melting at 211—212° (uncorr.). A. H.

Normal Diazo-metallic Salts. By ARTHUR R. HANTZSCH and DIMITER GERILOWSKI (*Ber.*, 1896, **29**, 1059—1066).—In reply to the criticism of Bamberger (this vol., i, 362), the authors maintain the accuracy of their statements as to the relative rates of decomposition of solutions of diazosulphanilic acid in the free state and in the presence of less than one equivalent of alkali. A. H.

Intramolecular re-arrangement of Diazonium Thiocyanates. By ARTHUR R. HANTZSCH and BENNO HIRSCH (*Ber.*, 1896, **29**, 947—952).—Diazonium thiocyanates are prepared from diazonium salts and potassium thiocyanate in alcoholic or aqueous solution; the solubility diminishes as the number of haloid elements in the benzene nucleus increases; they resemble the diazonium salts in general properties, but differ from the diazo-cyanides. Diazonium thiocyanates, containing one or more haloid elements in the benzene nucleus, undergo, more or less readily, intramolecular re-arrangement, the haloid atom changing place with the group SCN; the resulting compounds are less strongly coloured and not nearly so explosive as the original thiocyanates.

Benzenediazonium thiocyanate, N:NPh·SCN, is prepared from potassium thiocyanate and benzenediazonium chloride in absolute alcoholic solution below 0°; it is a yellow, highly explosive compound, moderately stable in aqueous solution; it readily combines with alkaline β -naphthol solution, and slowly decomposes into phenol, nitrogen, and hydrogen thiocyanate. *Parachlorobenzenediazonium thiocyanate*, prepared in a similar manner to the preceding compound from neutral parachlorobenzenediazonium chloride (see below), is much less soluble, and does not explode so readily; it may be filtered, and rubbed on a porous plate if moist, but when almost dry it decomposes with great ease.

Parathiocyanobenzenediazonium chloride, $\text{NCS} \cdot \text{C}_6\text{H}_4 \cdot \text{NCl} : \text{N}$, is formed almost instantaneously by adding a few drops of hydrochloric acid to the preceding compound in alcoholic solution; it crystallises in yellow plates, softens at 104° , explodes at 110 — 114° , and decomposes slowly at the ordinary temperature. *Parachlorothiocyano benzene*, $\text{NCS} \cdot \text{C}_6\text{H}_4\text{Cl}$, is obtained by the action of cuprous chloride on the diazonium chloride; it crystallises in colourless needles, melts at 35 — 36° , and is readily soluble; its vapour quickly attacks the eyes. This is the first instance of the preparation of a solid thiocyanate of the benzene series. *Tribromobenzenediazonium thiocyanate*, $\text{N} : \text{N}(\text{C}_6\text{H}_2\text{Br}_3) \cdot \text{SCN}$, may, owing to its sparing solubility, be prepared in aqueous solution. Neutral parachlorobenzenediazonium chloride is obtained by the action of amyl nitrite and a little anhydrous hydrogen chloride on parachloraniline hydrochloride in presence of absolute alcohol; the salt, after repeated solution in alcohol and precipitation with ether, softens at 60° , melts and decomposes at 70° , and is very hygroscopic. J. B. T.

Diazonium. By ARTHUR R. HANTZSCH (*Ber.*, 1896, **29**, 1067—1074).—The diazonium group must be taken to correspond with the ammonium group and the alkali metals, since it forms neutral and strongly dissociated salts with the strong acids, and also forms stable salts with weak acids. Its behaviour is in every respect analogous to that of the quaternary ammonium bases. Like the ammonium group, it is extremely unstable in the absence of acid ions. Hydroxyl ions convert it into the syndiazo-group.

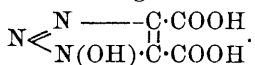
Three classes of diazo-compounds are now to be distinguished. The diazonium compounds, which have the constitution $\text{Ph} \cdot \text{N} \text{X} : \text{N}$, the syndiazo-compounds, $\begin{array}{c} \text{Ph} \cdot \text{N} \\ || \\ \text{R} \cdot \text{N} \end{array}$, and the antidiazo-compound, $\begin{array}{c} \text{Ph} \cdot \text{N} \\ || \\ \text{N} \cdot \text{R} \end{array}$. A. H.

Unsymmetrical α -Phenylhydrazine Compounds. By HANS RUPE (*Ber.*, 1896, **29**, 829).—Unsymmetrical *ethylic phenylhydrazidoformate*, $\text{NH}_2 \cdot \text{NPh} \cdot \text{COOEt}$, can be obtained by treating acetylphenylhydrazine with ethylic chloroformate, and hydrolysing the resulting acetyl compound. Its *benzylidene derivative* melts at 96 — 97° ; with cyanic acid, it yields *ethylic phenylsemicarbazidecarboxylate*, $\text{NH}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{NPh} \cdot \text{COOEt}$, which melts at 165 — 166° , and condenses, under the influence of zinc chloride, to phenylurazole, $\begin{array}{c} \text{CO} \cdot \text{NH} \\ | \\ \text{NH} \cdot \text{CO} \end{array} > \text{NPh}$; its *hydrochloride* yields with potassium thiocyanate a *thiocarbamide* melting at 221° ; and it condenses with carbonyl chloride to form *ethylic diphenylcarbazidodicarboxylate*, $\text{CO}(\text{NH} \cdot \text{NPh} \cdot \text{COOEt})_2$, which melts at 159° , and is converted by warming with alkalis into a *tetrazine derivative*, $\text{OH} \cdot \text{C} < \begin{array}{c} \text{N} - \text{NPh} \\ | \\ \text{NH} \cdot \text{NPh} \end{array} > \text{CO}$, which melts at 263 — 264° .

C. F. B.

Orthodinitroso-derivatives of the Benzene Series. By THEODOR ZINCKE (*J. pr. Chem.*, 1896, [2], **53**, 340—343).—By heating benzeneazimidole (Nietzki, *Abstr.*, 1895, i, 135) with hydriodic

acid, it is converted into azimidobenzene; by oxidation with potassium permanganate, it yields a strong tribasic acid,



Orthonitrohydrazines are easily converted by nitrous acid into orthonitrodiazoimides, and these lose two atoms of nitrogen when heated, yielding characteristic compounds which appear to be orthodinitroso-derivatives; the following have been prepared: *orthodinitrosobenzene*, $\text{C}_6\text{H}_4(\text{NO})_2$ (m. p. 71°); *orthodinitrosotoluenes*, $[\text{Me} : (\text{NO})_2 = 1 : 3 : 4 \text{ and } 1 : 2 : 3 \text{ respectively}]$ (m. p. $96-97^\circ$ and 60° respectively); *orthodinitroso-xylene*, $[\text{Me}_2 : (\text{NO})_2 = 1 : 3 : 4 : 5]$ (m. p. $108-109^\circ$). Reducing agents convert these dinitroso-compounds into diamines, ortho-dioximes, apparently, being intermediate products. *Benzeneorthodioxime*, $\text{C}_6\text{H}_4(\text{N} \cdot \text{OH})_2$, crystallises in yellowish needles, melts at 142° , and combines with both acids and bases to form intensely red salts; on oxidation, it yields dinitrosobenzene, and on treatment with hot alkalis, it gives an anhydride, $\text{C}_6\text{H}_4 \cdot \text{N} \begin{array}{c} \text{N} \\ \text{N} \end{array} \text{O}$, which yields an acid, probably furazanedicarboxylic acid, on oxidation.

A. G. B.

Reduction of the Nitro- to the Hydroxylamine Group. By EUGEN BAMBERGER and MAJA KNECHT (*Ber.*, 1896, **29**, 863—864).—The preparation of hydroxylamine derivatives from nitro-compounds may be carried out by the use of aluminium sulphate and a 5 per cent. zinc amalgam with excellent results. Nitrobenzene thus yields 85 per cent. of the theoretical yield (compare Wislicenus, this vol., i, 298).

A. H.

Stereoisomeric Benzhydroximic acid Derivatives. By ALFRED WERNER (*Ber.*, 1896, **29**, 1146—1153).—Lossen's criticisms (*Abstr.*, 1895, i, 37) of the author's previous work are answered. Three modifications of methylbenzhydroximic acid are known, one (m. p. 64°) was prepared by Lossen and Zanni, and termed the α -acid. Lossen has since failed to prepare it, but it proves to be the anti-compound (compare following abstract); the second melts at 44° , and is the syn-compound; the third, Lossen's β -acid, melts at 101° . The relationship between the α - and β -acids is very intimate; the α - is converted into the β -compound by the slightest trace of the latter, therefore special care is necessary in working with the α -compound, as the room, the atmosphere, and the clothes of the experimenter, must be perfectly free from the β -acid. Both compounds yield identical derivatives, and the α -acid is regenerated from these if the above precautions are observed. The molecular weight of the β -acid, in ethereal and in glacial acetic acid solution, corresponds with the simple formula.

J. B. T.

Stereoisomeric Derivatives of Benzhydroximic acid. By ALFRED WERNER and J. SUBAK (*Ber.*, 1896, **29**, 1153—1161; compare preceding abstract).—Methylantibenzhydroximic acid is prepared from benzimidomethyl ether and hydroxylamine; a mixture of two

acids is first obtained, which may either be separated in the manner described below, or converted by means of the benzoyl derivative into the anti-acid (m. p. 64°); by the action of phosphorus pentachloride, it yields an *ethereal phosphate*, $\text{PO}(\text{O}\cdot\text{N}\cdot\text{CPh}\cdot\text{OMe})_3$, which is crystalline, melts at 83° , and indicates that the compound has the anti-configuration; $\begin{array}{c} \text{Ph}\cdot\text{C}\cdot\text{OMe} \\ || \\ \text{N}\cdot\text{OH} \end{array}$. The benzoyl derivative crystallises in small needles, melting at 54° , and has been previously prepared by Lossen (Abstr., 1895, i, 37). The *benzenesulphonate*,



crystallises in needles, melting at 72° . The *dinitrophenyl* derivative, $\text{OMe}\cdot\text{CPh}\cdot\text{NO}\cdot\text{C}_6\text{H}_3(\text{NO}_2)_2$ [$\text{O}:\text{NO}_2:\text{NO}_2 = 1:2:4$], crystallises in slender, pale yellow needles, melting at 121° . The *paramethoxybenzoyl*- and *carbanilido*-derivatives are crystalline, and melt at 55° and 115° respectively.

The methylbenzhydroxamic acid prepared by Lossen from methylic iodide and silver benzoylbenzhydroximate (dibenzhydroximate) which melts at 63° , is a mixture of both stereoisomerides; these are separated by dissolving the acid in potash, and extracting the solution about 30 times with ether; the anti-acid dissolves first, then a mixture of both, and finally the *syn-acid*; this crystallises in small needles, melts at 44° , and slowly liquefies at the ordinary temperature, a portion changing into the anti-compound. By the action of phosphorus pentachloride, a chloro-derivative is obtained, which undergoes Beckmann's reaction, and, with sulphuric acid, is resolved into aniline, methylic benzoate, phenylmethylethane, hydrogen chloride, and carbonic anhydride, thus proving the configuration of the original acid to be $\begin{array}{c} \text{Ph}\cdot\text{C}\cdot\text{OMe} \\ || \\ \text{OH}\cdot\text{N} \end{array}$.

The *benzoyl* derivative, prepared in presence of potash in large excess, is crystalline, and melts at 55° . The 1:2:4-*dinitrophenyl* derivative is more readily soluble in light petroleum than the anti-compound; it crystallises in yellow needles, melting at 122 – 125° ; a mixture of both isomerides melts about 20° lower. The *paramethoxybenzoyl* derivative crystallises in colourless plates, melting at 96 – 98° . The *carbanilido*-derivative is crystalline, and melts at 117° ; when mixed with the anti-compound, the melting point falls about 20° . J. B. T.

Ethylenedihydroxylamine. By ALFRED WERNER and A. GEMSEUS (*Ber.*, 29, 1896, 1161–1164).—Benzenylamidoxime ethylenic ether, $\text{C}_2\text{H}_4(\text{O}\cdot\text{N}\cdot\text{CPh}\cdot\text{NH}_2)_2$, prepared from benzenylamidoxime, sodium ethoxide, and ethylenic bromide, crystallises from dilute alcohol in lustrous plates, which melt at 161° , and not at 155 – 156° , as previously stated. The *dichloro*-derivative,



is formed by the action of hydrochloric acid and sodium nitrite on the preceding compound; it crystallises in prisms, and melts at 59 – 60° . The *dibromo*-derivative, prepared in a similar manner by means of hydrobromic acid, crystallises from a mixture of alcohol and ether in

long, thin, silky, lustrous needles, melting at 100° ; by prolonged contact with water it is converted into an isomeric modification, which is also formed in small quantity with the original substance; the isomeride is readily soluble in ether, crystallises from glacial acetic acid in needles, and melts at $81-82^{\circ}$. *Ethylene ethylbenzhydroximate*, $C_2H_4(O\cdot N:CPh\cdot OEt)_2$, is obtained by the action of sodium ethoxide on either of the above haloid compounds; it is a brownish oil, with an aromatic odour, and was not completely purified; when hydrolysed by means of concentrated hydrochloric acid, it yields benzoic acid, and *ethylenedihydroxylamine hydrochloride*, $C_2H_4(O\cdot NH_2)_2\cdot 2HCl$, which crystallises in plates.

J. B. T.

Preparation of Valeranilide using Phosphorus Trichloride.

By ENRICO SPIZZICHINO and CARLO CONTI (*L'Orosi*, 1895, **18**, 262—263).—*Valeranilide*, $C_3H_7\cdot CH_2\cdot CO\cdot NHPh$, is readily obtained with development of heat by slowly adding phosphorus trichloride to a mixture of aniline and valeric acid; it crystallises from alcohol in beautiful white, odourless needles, melting at $103-105^{\circ}$. It is soluble in alcohol, ether, or chloroform, but insoluble in water, and is hydrolysed on fusion with potash.

W. J. P.

Products of the Chlorination of Benzaldehyde and their Derivatives.

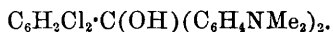
By ROBERT GNEHM and E. BÄNZIGER (*Ber.*, 1896, **29**, 875—878).—When benzaldehyde is treated with iodine and antimony pentachloride (American patent, No. 315,932), the product contains ortho- and meta-chlorobenzaldehyde, 3:4- and 2:5-dichlorobenzaldehyde, and perchlorobenzene. A certain amount of tetrachlorobenzene is formed during the fractionation of the chloraldehydes. The following derivatives of 2:5-dichlorobenzaldehyde were prepared. The *phenylhydrazone* melts at $104-105^{\circ}$; the *aniline compound* crystallises in white, nacreous plates, melting at $71\cdot 5-72^{\circ}$; the *paraphenetidine compound* melts at 59° ; the *methylamine compound* crystallises in nacreous plates, and melts at 52° . The aldehyde forms a condensation product with dimethylaniline, which is the *leuco-base* of the colouring matter contained in "new solid green 3B"; it crystallises from benzene in vitreous plates, and melts at 179° .

2:5-Dichlorobenzaldehyde is converted by nitration into orthonitrodichlorobenzaldehyde [$CHO : Cl_2 : NO_2 = 1 : 2 : 5 : 6$] (*Ber.*, **17**, 752), and an isomeric substance melting at $66\cdot 5^{\circ}$. The latter yields an *oxime*, which crystallises in long, white needles, melting at 93° , and a *phenylhydrazone*, which forms slender, orange-coloured needles, and melts at 174° . The *aniline compound* crystallises in faintly yellow, thin tablets, and melts at $113-114^{\circ}$.

The *oxime* of orthonitrodichlorobenzaldehyde crystallises in long, white needles, and melts at $154-155^{\circ}$; the *phenylhydrazone* forms slender needles, melting at $146-147^{\circ}$, and the *aniline compound* melts at $102-103^{\circ}$. Orthonitrodichlorobenzaldehyde can readily be reduced to the corresponding amido-derivative, which yields an *oxime*, melting at $175-176^{\circ}$, and a *phenylhydrazone*, melting at $102-103^{\circ}$. This base could not be converted into a hydroxy-compound by means of the diazo-reaction.

When the orthonitro-compound is treated with sodium sulphite, the nitro-group is eliminated, and a substance is formed which does not contain nitrogen.

The mixture of chloraldehydes which is referred to above is used for the manufacture of colouring matters. "New solid green 3B" is a mixture of the nitrate and hydrochloride of the colour base derived from tetramethyldiamidodichlorotriphenylcarbinol,



"New solid green 2B" consists of a mixture of the hydrochloride just mentioned, and the corresponding monochloro-derivative. "Firn blau" is the hydrochloride of the colour base of dimethyldiamidodiorthotolyldichlorophenylcarbinol.
A. H.

Preparation of Mono- and Di-acetyl Derivatives of Aromatic Hydrocarbons. By VICTOR MEYER (*Ber.*, 1896, 29, 846—848).—The use of the method previously given by Meyer and Baum (this vol., i, 228) for the preparation of monacetyl derivatives sometimes resulted in the formation of diacetyl derivatives. In order to avoid this, it is advisable to vary the amount of aluminium chloride employed in the two cases, instead of the time of heating as was previously done.

The constitution of diacetylisodurene has been confirmed by the author in conjunction with Seymour, so that this substance is a 1:5-diketone.
A. H.

New Experiments on the Law of Formation of Oximes, Hydrazones, and Ethereal Salts. By VICTOR MEYER (*Ber.*, 1896, 29, 830—839).—Many of Claus' statements (*Abstr.*, 1888, 275; and this vol., i, 230) are entirely erroneous. Acetylisodurene [$\text{Me}_4:\text{Ac} = 1:3:4:5:6$] yields neither a hydrazone nor an oxime. Acetyldurene [$1:2:4:5:6$] melts at 73° (Claus 63°) and does not form a hydrazone. Durenecarboxylic acid [$\text{Me}_4:\text{COOH} = 1:2:4:5:6$] was prepared long ago by Jacobsen (*Abstr.*, 1889, 877), and does not melt at 127° , but at 178° ; it is not readily etherified, but it yields 60 per cent. of the methylic salt when treated with gaseous hydrogen chloride in boiling methyl alcoholic solution. Isodurenecarboxylic acid [$1:3:4:5:6$] is not an oil, but forms good crystals, and melts, even in the crude state, above 150° .

The influence of the grouping $\text{C}_6\text{H}_3\text{Me}_2\cdot\text{CO}\cdot\text{R}$, [$\text{CO}:\text{Me}_2 = 1:2:6$] on the power to form an oxime or hydrazone has been studied, in the case of mesitylene derivatives, $\text{C}_6\text{H}_2\text{Me}_3\cdot\text{CO}\cdot\text{R}$. When $\text{R} = \text{H}$, or COOH , oximes and hydrazones are formed; these are not formed when $\text{R} = \text{Me}$, Et , Pr^a , P^b , Ph , CH_2Cl , CHCl_2 , CCl_3 , $\text{CH}_2\cdot\text{CH}_2\cdot\text{COOH}$.

Alkylic mesitylgyoxylates do really yield oximes (compare Baum, this vol., i, 222); this was shown by preparing the oxime of the amylic salt, the analysis of which leaves no doubt as to its composition.

Mesitylenecarboxylic acid (compare this vol., i, 228), when gaseous hydrogen chloride is passed through its alcoholic solution
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at 0°, yields in seven days and nights, 26 per cent., in double the time 46 per cent., of ethereal salt. Symmetrical trinitrobenzoic acid yields no methylic salt, even when treated for 30 days in this way. It appears that the groups OH and Me in the ortho-positions retard the formation of an ethereal salt, whilst Cl, Br, I, NO₂ prevent it altogether.

C. F. B.

Fluorine and the Law of Etherification. By J. VAN LOON and VICTOR MEYER (*Ber.*, 1896, 29, 839—845).—It was thought probable, from stereochemical considerations, that the influence of fluorine might not resemble that of the chemically similar radicles Cl, Br, I, and NO₂ (compare preceding abstract), but rather approximate to that of Me and OH, which, like it, have a low atomic weight, although their chemical character is different. This was confirmed by experiment; the acid, NO₂·C₆H₃F·COOH [COOH : F : NO₂ = 1 : 2 : 6] yields no ethereal salt when treated with alcoholic hydrogen chloride in the cold; but it yields 67 per cent. when gaseous hydrogen chloride is passed through its boiling alcoholic solution, under which circumstances the corresponding acid containing Cl in place of F yields no ethereal salt. The radicle F thus resembles Me and OH in that, when present in the ortho-position relatively to the COOH group, it only retards the formation of an ethereal salt, and does not, like Cl, Br, I, and NO₂, altogether prevent it.

It is pointed out that in stereochemical considerations, we are not concerned with molecular volumes in the sense understood by Kopp. With certain reservations, the atomic weight of a radicle conditions its stereochemical action. But the radicle cetyl, CH₂·[CH₂]₁₄·CH₃, does not resemble the heavy radicles I, &c., in its influence on etherification, but has the same influence as the light radicle CH₃, only that CH₂ group nearest to the benzene ring coming into play. The radicle NO₂, however, acts with its whole weight, and not by virtue of the N atom alone, which would necessitate its being classed with the light radicles.

C. F. B.

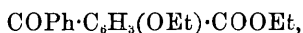
A New Method of Formation of Trimethylmandelic [symmetrical Trimethylphenylacetic] acid. By VICTOR MEYER and CARL SOHN (*Ber.*, 1896, 29, 846).—When acetomesitylene is reduced with faintly alkaline potassium permanganate solution, symmetrical trimethylphenylacetic acid is sometimes formed, under conditions which have not been definitely ascertained, instead of mesitylgyoxylic acid, which is the usual product of the action.

A. H.

Dry Distillation of Calcium Phenylsalicylate [Orthophen-oxybenzoate]. By BERTHOLD JEITELES (*Monatsh.*, 1896, 17, 65—67).—Calcium orthophenoxycarboxylate is distilled in an atmosphere of hydrogen; the product is treated with soda, which dissolves some quantity of phenol, and extracted with ether. On evaporation, the ethereal extract yields a substance crystallising from dilute alcohol in long needles melting at 172—173°, and a yellow oil boiling at 248—251°.

The former substance proves to be xanthone $C_6H_4 \begin{smallmatrix} \diagup CO \\ \diagdown O \end{smallmatrix} C_6H_4$, and the latter is identical with phenylic ether $(C_6H_5)_2O$. A. L.

Benzoylsalicylic acid. By HEINRICH LIMPRICHT (*Annalen*, **290**, 164—171).—*Parabenzoylsalicylic acid*, $COPh \cdot C_6H_3(OH) \cdot COOH$, is obtained in the form of an alkylic salt when benzoic chloride acts on ethereal salts of salicylic acid in carbon bisulphide solution under the influence of aluminium chloride; it crystallises from alcohol in slender needles, and melts at 210° . Ferric chloride develops a violet coloration in the aqueous solution, and when the dry substance is distilled from lime, parahydroxybenzophenone is produced. The *barium hydrogen* salt crystallises in leaflets, and the *barium* salt in green needles. The *meihylic* and *ethylic* salts melt at 92° and 97° respectively, and the latter gives rise to the *potassium* derivative which crystallises in greenish-yellow leaflets; ethylic iodide converts the potassium compound into the *ethyl* derivative,



which crystallises from petroleum in aggregates of needles, and melts at 56° . The *ethyl* derivative of benzoylsalicylic acid, *parabenzoylorthoethoxybenzoic acid*, $COPh \cdot C_6H_3(OEt) \cdot COOH$, is obtained from the foregoing compound by hydrolysis; it crystallises from dilute spirit in small needles, and melts at 109° .

Phenylic benzoylsalicylate (*benzoylsalol*), $COPh \cdot C_6H_3(OH) \cdot COOPh$, is obtained by heating benzoylsalicylic acid and phenol with phosphorus oxychloride; it crystallises in lustrous, monoclinic plates, and melts at 84° . The *benzoic* derivative of ethylic salicylate, $OBz \cdot C_6H_4 \cdot COOEt$, is produced on heating ethylic orthoethoxybenzoate with benzoic chloride, carbon bisulphide, and aluminium chloride; it crystallises in large, colourless plates melting at 79° , and is identical with Freer's ethylic benzoylsalicylate (*Abstr.*, 1893, i, 66). The *benzoic* derivative of ethylic benzoylsalicylate, $COPh \cdot C_6H_3(OBz) \cdot COOEt$, is obtained from benzoic chloride and the sodium derivative of ethylic benzoylsalicylate; it crystallises in leaflets, and melts at 87° .

Metanitroparabenzoylsalicylic acid is obtained in the form of its ethylic salt when ethylic salicylate, carbon bisulphide, and metanitrobenzoic chloride are heated with aluminium chloride; it crystallises in small, lustrous prisms, and melts at 244° . The *ethylic* salt, to which reference has been made, crystallises in transparent leaflets, and melts at 116° .

Ethylic metahydroxybenzoate and its potassium and ethyl derivatives, when treated with benzoic chloride and aluminium chloride, yield the *compound*, $OBz \cdot C_6H_4 \cdot COOEt$, which crystallises from alcohol in long, white needles, and melts at 58° ; boiling caustic soda gives rise to benzoic and metahydroxybenzoic acids. M. O. F.

Reaction of Aromatic Bases with Ethylic Benzylidenemalonate and Furfurylidenemalonate. By I. GOLDSTEIN (*Ber.*, 1896, **29**, 813—818; compare *Abstr.*, 1895, i, 470).—Ethylic benzyl-

idenemalonate forms, with unsymmetrical methylphenylhydrazine, a crystalline additive compound, *ethylic β-phenylmethylhydrazidobenzylmalonate*, $\text{NMePh}\cdot\text{NH}\cdot\text{CHPh}\cdot\text{CH}(\text{COOEt})_2$. This yields a *hydrochloride*, which is decomposed by water; hydrolysis converts it into the *dipotassium salt*, but when an attempt is made to liberate the acid from this salt, benzylidenemethylhydrazine, $\text{NMePh}\cdot\text{N}\cdot\text{CHPh}$, and malonic acid are obtained instead. A similar additive compound, *ethylic β-piperidobenzylmalonate*, $\text{C}_6\text{NH}_{10}\cdot\text{CHPh}\cdot\text{CH}(\text{COOEt})_2$, melting at $58-59^\circ$, is formed with piperidine; the *hydrochloride* and *dipotassium salt* were prepared, but the free acid does not exist; it breaks up into piperidine, benzaldehyde, and malonic acid. This additive-compound yields a *tri-sodium salt* when treated with alcoholic sodium ethoxide, which shows that, in the process of addition, the hydrogen atom must have gone to the α -carbon atom. With coniine, ethylic benzylidenemalonate yields *ethylic phenylpropyltetrahydroazindonecarboxylate*,
$$\begin{array}{c} \text{CH}_2\cdot\text{CHPr}\cdot\text{N}\cdot\text{CHPh} \\ \text{CH}_2\cdot\text{CH}_2-\text{CH}-\text{CO} \end{array} > \text{CH}\cdot\text{COOEt}$$
. This melts at $150-152^\circ$; its *platinochloride* and *aurochloride* were prepared. The free acid melts at 85° , and at 95° loses carbonic anhydride, forming *phenylpropyltetrahydroazindone*, which melts at 212° ; the *lead salt* of the acid crystallises with H_2O .

Piperidine also forms, with ethylic furfurylidenemalonate, an additive compound, $\text{C}_4\text{OH}_7\cdot\text{CH}(\text{C}_5\text{NH}_{10})\cdot\text{CH}(\text{COOEt})_2$, which melts at $35-37^\circ$.
C. F. B.

Ethylic α - and β -Benzoyltricarballates. By WILLIAM O. EMERY (*J. pr. Chem.*, 1896, [2], 53, 312-314).—*Ethylic α -benzoyltricarballate*, $\text{COOEt}\cdot\text{CHBz}\cdot\text{CH}(\text{COOEt})\cdot\text{CH}_2\cdot\text{COOEt}$, is prepared by heating a mixture of sodium (2.4 grams) dissolved in absolute alcohol (30 grams), ethylic benzoylacetate (20 grams), and ethylic chlorosuccinate (22 grams), on the water bath for half an hour. It is a greenish, fluorescent oil which distils at 250° (at 16 mm.), and has a sp. gr. = 1.14557 at $20^\circ/4^\circ$; strong hydrochloric acid converts it into phenacylsuccinic acid (m. p. $156-157^\circ$) which yields an anhydride, $\text{C}_{12}\text{H}_{10}\text{O}_4$, melting at $147-148^\circ$, and is obtainable by other methods to be elucidated presently.

Ethylic β -benzoyltricarballate, $\text{COOEt}\cdot\text{CBz}(\text{CH}_2\cdot\text{COOEt})_2$, is similarly prepared from sodium ethoxide, ethylic benzoylsuccinate, and ethylic bromacetate. It is a light, yellow oil which boils at 225° (at 14 mm.); its sp. gr. = 1.14783 at $20^\circ/4^\circ$. Prolonged heating with strong hydrochloric acid converts it into β -benzoylglutaric acid.

A. G. B.

Dicarboxyphenylglyoxylic acid. By CARL GRAEBE and FR. BOSSEL (*Annalen*, 1896, 290, 206-216; compare Abstr., 1893, i, 593).—The *barium* and *calcium* salts of dicarboxyphenylglyoxylic acid contain $4\text{H}_2\text{O}$, the *potassium salt* crystallises from water in leaflets, and the *silver salt* is sparingly soluble in water; the *dimethylic* and *trimethylic* salts melt at $154-156^\circ$ and 168° , respectively. The phenylhydrazone (*loc. cit.*) crystallises in colourless leaflets, and melts at $205-208^\circ$.
M. O. F.

Hemimellitic acid. By CARL GRAEBE and MAX LEONHARDT (*Annalen*, 1896, **290**, 217--238).—Graebe and Bossel have shown that hemimellitic acid is produced on oxidising dicarboxyphenylglyoxylic acid (Abstr., 1893, i, 593; also foregoing abstract), which, therefore, is a convenient source of the acid in question.

Hemimellitic acid crystallises from water in plates, containing $2\text{H}_2\text{O}$; it melts at 190° , being converted into the *anhydride* $\text{C}_9\text{H}_4\text{O}_5$, which melts at 196° , and yields carbonic and phthalic anhydrides above 300° . The *monopotassium* salt is precipitated in leaflets on adding aqueous potassium chloride to a cold, saturated solution of the acid; it contains $2\text{H}_2\text{O}$, and dissolves in 170 parts of water at 17° . The *tripotassium* salt crystallises in needles, and dissolves very readily in water; the barium salt contains $6\text{H}_2\text{O}$.

Although, in accordance with Victor Meyer's generalisation, direct etherification of hemimellitic acid gives rise to the dimethylic salt alone, methylic alcohol converts the anhydride into a monomethylic salt, whilst further action of the alcohol, under the influence of hydrogen chloride, leads to the trimethylic salt. The *monomethylic* salt crystallises from water in needles, and melts at $203\text{--}205^\circ$, the *dimethylic* salt melts at 145° , and does not decompose when distilled, and the *trimethylic* salt melts at 100° .

The *imide* of hemimellitic acid, $\text{COOH}\cdot\text{C}_6\text{H}_3<\begin{smallmatrix}\text{CO}\\\text{CO}\end{smallmatrix}>\text{NH}$, is obtained by the action of ammonia on the anhydride, and crystallises from water in colourless needles melting at 247° (corr.). The *silver* salt is colourless, and the *calcium* salt crystallises in leaflets, and contains $1\frac{1}{2}\text{H}_2\text{O}$.

Benzoylphthalic acid [$\text{COOH}_2 : \text{COPh} = 1 : 2 : 3$] is obtained by heating the anhydride of hemimellitic acid with aluminium chloride and benzene in a reflux apparatus; it crystallises from water in colourless needles containing $1\text{H}_2\text{O}$, and effervesces at $130\text{--}140^\circ$, yielding the *anhydride* which melts at 183° (corr.). The solution in cold concentrated sulphuric acid is bright yellow, becoming olive-green at $145\text{--}150^\circ$, 1-anthraquinonecarboxylic acid being formed; this substance melts at $293\text{--}294^\circ$ (corr.), and the *ethylic* salt crystallises from alcohol in yellow needles melting at 169° . *Benzoyliso-phthalic acid* [$\text{COOH} : \text{COPh} : \text{COOH} = 1 : 2 : 3$] is prepared by heating monopotassium hemimellitate with aluminium chloride and benzene, and crystallises from dilute alcohol in needles melting at 260° ; concentrated sulphuric acid converts it into 1-anthraquinonecarboxylic acid. *Dibenzoylbenzoic acid* [$\text{COOH} : \text{COPh}_2 = 1 : 2 : 3$] is produced along with benzoylphthalic acid, and melts at 208° ; phthalophenone is formed on submitting the substance to dry distillation. *Dibenzoylbenzoic acid* [$\text{COOH} : \text{COPh}_2 = 1 : 2 : 6$] is obtained when the action of benzene and aluminium chloride extends over a shorter period; it melts at 100° .

When hemimellitic anhydride is heated with resorcinol for two hours at 200° , two fluoresceincarboxylic acids are produced, one of which yields an anhydride; on extracting the powdered mass with boiling water, and, on cooling, the 6-fluoresceincarboxylic acid, $\text{C}_{21}\text{H}_{12}\text{O}_7$, is deposited in yellow needles; it does not melt at 280° , and the solu-

tions in alkalis exhibit very feeble fluorescence. The *anhydride* of 3-fluoresceincarboxylic acid, $C_{21}H_{10}O_6$, is obtained by dissolving the residue in sodium carbonate and precipitating with hydrochloric acid; the solutions in alkalis are yellowish-red, and exhibit feeble fluorescence. The *acetyl* derivative is crystalline, and melts above 300° .

When hemimellitic anhydride is heated with metadimethylamido-phenol, a *rhodamine* is produced which dissolves in alkalis forming a violet-red solution. M. O. F.

Derivatives of Sulphometabromobenzoic acid. By CARL BOETTINGER (*Arch. Pharm.*, 1896, **234**, 47—55).—*Chlorosulphometabromobenzoic chloride*, $SO_2Cl \cdot C_6H_3Br \cdot COCl$ [5 : 3 : 1], is prepared by heating potassium or calcium sulphometabromobenzoic acid with phosphorus pentachloride, dissolving in ether, and washing out the phosphorus oxychloride with water; it crystallises in long, colourless needles, and melts at 64° . The *amido*-derivative,



forms hard, glistening crystals, with $1H_2O$, and, when anhydrous, melts at 198.5 — 199.5° . By heating it with dilute caustic soda solution, it is converted into *sodium sulphamidometabromobenzoate*; the free acid crystallises in long, colourless needles, and melts at 251° . On acidification, the mother liquor from the crystallisation of the diamide yields a second *amido*-acid which crystallises in thick prisms, and melts at 237 — 238° .

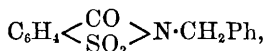
Chlorosulphometabromobenzoic acid can be isolated from the mass obtained in preparing the foregoing chloride; it forms thick, white crystals, melts at 170° , and is nearly insoluble in light petroleum, sparingly soluble in cold alcohol, and more freely in ether.

Sulphimetabromobenzoic acid, $SO_2H \cdot C_6H_3Br \cdot COOH$, is obtained by reducing chlorosulphometabromobenzoic acid with zinc dust in alcoholic solution. It crystallises from hot water in slender needles, and melts at 202° .

A postscript contains some remarks on Heyl and V. Meyer's recent paper on the benzene problem (this vol., i, 145).

A. G. B.

Derivatives of Orthobenzoicsulphinide (Saccharin). By HUGO ECKENROTH and GEORG KOERPEN (*Ber.*, 1896, **29**, 1048—1051; compare this vol., i, 304).—*Benzylorthobenzoicsulphinide*,



crystallises in colourless needles melting at 118° , and has not a sweet taste. *Benzylorthamidodisulphobenzoic acid*, $COOH \cdot C_6H_4 \cdot SO_2 \cdot NH \cdot CH_2Ph$, is an uncrystallisable oil; the *sodium salt* crystallises in rosettes of small needles, and the *barium salt* is a crystalline powder. *Paranitrobenzylorthobenzoicsulphinide* forms slender, light yellow needles, and melts at 175.5 — 176° . *Paranitrobenzylorthamidodisulphobenzoic acid* forms yellowish crystals, and melts at about 170° ; the *potassium salt* crystallises in colourless rhomboids. *Acetylorthobenzoicsulphinide* is

formed by the action of acetic anhydride on sodium benzoicsulphinide, whilst benzoicsulphinide itself is always formed by the action of acetic chloride. It crystallises in white, lustrous plates, and, when warmed with aqueous soda, yields sodium acetate and benzoicsulphinide, and not a sulphobenzoic acid. When sodium benzoicsulphinide is heated with ethylenic bromide and a little alcohol, it yields ethylenediorthobenzoicsulphinide in small quantity, along with *bromethylortho-benzoicsulphinide*, $C_6H_4 < \begin{smallmatrix} SO_2 \\ CO \end{smallmatrix} > N \cdot C_2H_4Br$. The latter crystallises in white needles melting at 96° . A. H.

Dissociation of Diazosulphonates [Correction]. By EUGEN BAMBERGER (*Ber.*, 1896, **29**, 1052).—The author points out that he was in error in his criticism (this vol., i, 373) of the calculation of certain of the results obtained by Hantzsch by means of the cryoscopic method (*Abstr.*, 1895, i, 664). A. H.

The Ionic Dissociation of the Diazosulphonates. By ARTHUR R. HANTZSCH and DIMITER GERILOWSKI (*Ber.*, 1896, **29**, 1057—1058; compare the foregoing abstract).—The criticism of Bamberger (this vol., i, 373) is founded on a miscalculation, the numbers obtained by the authors being perfectly correct. A. H.

Stereoisomeric Salts of Orthodiazobenzenesulphonic acid. By DIMITER GERILOWSKI (*Ber.*, 1896, **29**, 1075—1078).—*Diazonium-benzeneorthosulphonic acid*, $N:N < \begin{smallmatrix} O \\ C_6H_4 \end{smallmatrix} > SO_2$, is a yellowish, crystalline substance, which is more readily soluble in water than the para-compound, and detonates gently when it is heated. *Sodium syndiazobenzenecorthosulphonate* is prepared in a manner similar to the corresponding para-salt (*Abstr.*, 1895, i, 664). It forms white, silky needles, and may be preserved in dry air, but becomes red, and then deliquesces in the atmosphere. It readily yields a colouring matter with β -naphthol, which produces a yellow shade of red. The *anti-salt* is more soluble in water than the *syn-salt*, and has not been obtained in the solid state.

Potassium syndiazobenzenecorthosulphonate, $SO_3K \cdot C_6H_4 \cdot N_2 \cdot OK + \frac{1}{2}H_2O$, is a yellowish powder. The *anti-salt*, obtained by boiling the *syn-salt* with the mother liquor from its preparation, crystallises in groups of radiating needles. As in the para-series, the two salts behave differently towards hydrochloric acid; the *syn-salt* is immediately converted into the diazonium-compound, whilst this change only occurs slowly with the *anti-salt*, the solution of which is, therefore, rendered acid by the addition of hydrochloric acid, and only slowly becomes neutral. A. H.

Preparation of Flavone Derivatives. By PAUL FRIEDLÄNDER and HERMANN RÜDT (*Ber.*, 1896, **29**, 878—880).—Benzaldehyde reacts with orthohydroxyacetophenone alcohols, or their chlorides to form condensation products which are closely related to the flavone derivatives, such as chrysin and the colouring matters of quercitron bark and fustic ("fustet.")

Dihydroxyflavone, $\begin{array}{c} \text{C(OH):C(OH) \cdot C \cdot O - CPh} \\ | \qquad \qquad \qquad | \\ \text{CH:CH} \text{---} \text{C} \cdot \text{CO} \cdot \text{CH} \end{array}$, is formed when gallochloracetophenone, $\text{C}_6\text{H}_2(\text{OH})_3 \cdot \text{CO} \cdot \text{CH}_2\text{Cl}$, is treated with benzaldehyde and aqueous potash. It forms lustrous, yellow plates, and dyes mordanted cloth; the colour being yellow with alumina, and brown with chromium mordants. The *acetyl* compound forms colourless crystals melting at $198\text{--}199^\circ$. Dihydroxyflavone is isomeric with chrysin, which is a derivative of phloroglucinol. This reaction occurs with a large number of hydroxyacetophenone derivatives, and is being further investigated. A. H.

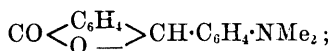
New Method of preparing Orthohydroxybenzophenone. By CARL GRAEBE and F. ULLMANN (*Ber.*, 1896, **29**, 824—825).—This compound is at once obtained by acting on methylsalicylic chloride, $\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{COCl}$, with benzene in the presence of aluminium chloride; prepared in this way, it melts at $39\text{--}40^\circ$. It yields xanthone when heated with lead oxide. Another substance, possibly a dihydroxybenzophenone, is formed at the same time as the monhydroxy-compound; it melts at 127° , and is only sparingly soluble in light petroleum. C. F. B.

Orthobenzoylphenol [**Orthohydroxybenzophenone**]. By PAUL COHN (*Monatsh.*, 1896, **17**, 102—109).—Phenylindoxazine is heated with fuming hydriodic acid (sp. gr. = 1.7) and phosphorus in sealed tubes at $140\text{--}160^\circ$ during 6—7 hours; the product is diluted with water, extracted with ether, the ethereal extract being then evaporated, and the residue heated on the water bath with sodium ethoxide. After desiccation, the powdered mass is extracted in a Soxhlet's apparatus with anhydrous ether, when the *sodium* derivative of orthobenzoylphenol, $\text{ONa} \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{C}_6\text{H}_5$, is dissolved, and crystallises in small, yellow needles; it dissolves readily in dilute alkali and alcohol, but only sparingly in ether. *Orthobenzoylphenol* [*orthohydroxybenzophenone*], $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{COPh}$, crystallises in leaflets, dissolves sparingly in water, but readily in alcohol, ether, and acetic acid; it melts at 36° , and distils, unaltered, under 560 mm. pressure; it has a characteristic odour, and forms sparingly soluble, yellow barium and calcium compounds; it is violently attacked by warm, dilute nitric acid, and yields explosive nitro-compounds when dissolved in a mixture of nitric and sulphuric acids. It yields salicylic acid when fused with potash.

Orthobenzoylphenol gives a number of characteristic derivatives. Its *dibromo*-derivative, $\text{OH} \cdot \text{C}_6\text{H}_2\text{Br}_2 \cdot \text{COPh}$, crystallises in beautiful, light-green needles, dissolves sparingly in cold alcohol, readily in hot alcohol and chloroform, and melts at 126° . *Orthomethoxybenzophenone*, $\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{COPh}$, formed by the action of methylic iodide at 100° on the potassium derivative, is a yellowish oil sparingly soluble in water and alkalis, readily soluble in alcohol, ether, &c. The *benzoate*, $\text{COPh} \cdot \text{C}_6\text{H}_4 \cdot \text{OBz}$, is readily obtained by the Baumann-Schotten method; it forms a yellowish oil which dissolves readily in all solvents, with the exception of water or alkalis. The *phenylhydrazone*, $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{CPh:N} \cdot \text{NHPh}$, is formed by the action of phenylhydrazine

on the phenol at 150° ; it is insoluble in water, acids, or alkalis, sparingly soluble in cold alcohol or ether, but readily in benzene and hot alcohol; from the latter, it crystallises in beautiful, transparent prisms, which have a tendency to aggregate in star-like forms; it melts at 155° . The *oxime*, $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CPh}\cdot\text{NOH}$, dissolves in alkalis, and crystallises from ether; it melts to a colourless liquid at $133\text{--}134^{\circ}$. A. L.

Condensation of Orthophthalaldehydic acid with Dimethylaniline. By ROBERT EBERT (*Chem. Zeit.*, 1895, 19, 2039—2040).—Orthophthalaldehydic acid (Racine, Abstr., 1886, 549) is readily soluble in dimethylaniline, and on treating the hot solution with a dehydrating agent, such as zinc chloride, hydrogen chloride, anhydrous oxalic acid, &c., a blue or green colour is developed. The product, after being dissolved in water or dilute acid, and treated with caustic soda, yields a resin, whilst Fischer's dimethylanilinephthalin remains in solution. The resin contains *dimethylamidophenylphthalide*,



this melts at 186° , is soluble in ether, benzene, and alcohol, and only sparingly soluble in 50 per cent. alcohol, from which it crystallises in colourless plates. It is readily soluble in hydrochloric acid, and is completely precipitated by alkalis. The solution of the base in sulphuric acid is colourless, but turns first yellow and then orange on warming.

The red or blue colouring matter obtained by the condensation of the aldehydic acid with dimethylaniline in the presence of zinc chloride is probably Fischer's phthalic green. J. J. S.

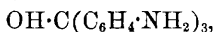
Coloured Rosaniline Bases. By GEORG VON GEORGIEVICS (*Monatsh.*, 1896, 17, 4—12; compare Abstr., 1895, ii, 257).—The colourless base of pararosaniline, $\text{C}_{19}\text{H}_{19}\text{N}_3\text{O}$, may be obtained by adding to a faintly acid solution of magenta (1 gram) in water at 70° (3 litres) a slight excess of alkali, rapidly filtering from the amorphous precipitate, and cooling the filtrate. It is obtained as beautiful shining leaflets, and when moist is stable only in presence of alkali, becoming coloured immediately on its removal. The red modification of the base is obtained on precipitating a cold solution of magenta by a little more than the calculated quantity of alkali, and contains neither chlorine nor carbonic anhydride. The red coloration is not due to the formation of a carbonate, as it becomes apparent even in the complete absence of carbonic anhydride, nor is it attended by any appreciable alteration in composition.

Although the colour of a solution of the coloured base is less intense than that of a corresponding solution of the hydrochloride, yet the dyeing powers of the two appear to be identical, equal weights of silk dyed to the same depth of colour in either solution extracting the same weight of base.

The coloured base, when repeatedly extracted with hot water, becomes darker in colour and less soluble in water. The final pro-

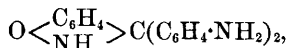
duct, which bears a marked resemblance to the original substance, gives on analysis numbers agreeing with the formula $C_{19}H_{17}N_3O$, and contains, therefore, two atoms of hydrogen less than the rosaniline base.

As a result of his experiments, the author concludes that there are three rosaniline bases: (1) a colourless carbinol base,



readily passing into (2) a magenta coloured ammonium base,

$\begin{matrix} C_6H_4 \\ OH \cdot NH_2 \end{matrix} > C(C_6H_4 \cdot NH_2)_2$, which is present in the aqueous solution of rosaniline salts, and (3) an imidoxide base,



which is more stable and less soluble in water than the ammonium base, and may be obtained from it by the action of hot water.

A. L.

Action of Bromine, Chlorine and Sulphur on Fluorene.

By CARL GRAEBE and B. VON MANTZ (*Annalen*, 1896, **290**, 238—246; compare Abstr., 1893, i, 38).—When bromine or chlorine acts on fluorene at 115—150°, the halogen enters a phenylene residue, whilst above this temperature methylenic hydrogen is eliminated, and bidiphenylenethylene is produced (*loc. cit.*). The dibromide of the hydrocarbon crystallises from boiling benzene or toluene in colourless plates, and melts and decomposes at 235°; the *dichloride*, $C_{26}H_{16}Cl_2$, also forms colourless crystals, and melts at 234°. Oxidation of bidiphenylenethylene with potassium dichromate and dilute sulphuric acid converts it into fluorenone along with a *compound*, $C_{30}H_{26}O_2$, which separates from glacial acetic acid in pale yellow crystals, and melts at 250—252°; when distilled from zinc dust, bidiphenylene-ethylene yields fluorene.

On heating fluorene with sulphur, hydrogen sulphide is evolved, and bidiphenylethane or bidiphenylethylene is produced according to the amount of sulphur employed.

M. O. F.

Action of Iodoform on β -Naphthol in Sunlight.

By M. C. SCHUYTEN (*Chem. Zeit.*, 1895, **19**, 2164).—When a concentrated ethereal solution of iodoform (1 mol.) is mixed in the dark with α -naphthol (5 mols.), and the resulting mixture exposed in a closely stoppered bottle to bright sunlight, a considerable quantity of a bronze coloured, crystalline substance is deposited, together with a small amount of iodoform. The latter, however, goes into solution again if the mixture is left exposed to sunlight for several days. The compound, after extracting with boiling alcohol and drying at 100°, forms glistening, bronzy crystals, and is only sparingly soluble in the usual solvents, but readily in chloroform. An alcoholic solution leaves dark green, rhombic crystals, which melt at 250—251° (uncorr.). When heated in a tube, it melts to a blue liquid, from which violet fumes of iodine are liberated. The iodine is readily removed from the molecule by warming with potash solution, by treatment with

phenylhydrazine, or by nascent hydrogen. Warm acetic acid and mineral acids dissolve the compound, yielding yellowish-green fluorescent solutions. The author thinks that the compound is to be regarded as *tolyldi-iodoketoindene*, $C_6H_4 < \begin{smallmatrix} CHI \\ CO- \end{smallmatrix} > CI \cdot C_6H_4Me$.

The product obtained by the action of dilute caustic soda on the above compound forms a red, amorphous powder, melts at 220° , and is probably *tolylketoindene*.

α -Naphthol does not react in the same manner.

J. J. S.

Derivatives of α -Naphthylamine. By CARL BOETTINGER (*Chem. Zeit.*, 1895, 19, 2080—2082; compare Abstr., 1895, i, 106).—A mixture of succino- α -naphthalide and succinonaphthil is obtained when succinic acid (1 mol.) is heated with α -naphthylamine ($1\frac{1}{2}$ mol.) in an oil bath at about 175° . The two are best separated by boiling alcohol. The α -naphthalide, $C_4H_4O_2(NH \cdot C_{10}H_7)_2$, is formed in small quantity; it is extremely sparingly soluble in boiling absolute alcohol, and melts at 275° (compare Hanamann, *Ber.*, 1877, 10, 1713, who gives the melting point as 285°). It may be distilled in a vacuum without undergoing decomposition, and when heated with acetic anhydride in a sealed tube at 140° , it is partially converted into a *diacetyl* derivative, which melts at 122° .

Succinonaphthil, $C_4H_4O_2 \cdot NC_{10}H_7$, crystallises from aqueous alcohol in long prisms or compact tetrahedra, and melts at 151.5 — 153° ; when warmed with alcoholic potash, it yields the potassium salt of α -naphthalidosuccinic acid (compare Hanamann).

Pyrotartaric acid reacts in very much the same way when heated with α -naphthylamine at 150° . The *dinaphthalide* of pyrotartaric acid is insoluble in ether, only sparingly soluble in boiling alcohol, and crystallises in long, colourless, hair-like needles, which melt at 243 — 244° . The corresponding *naphthil* is readily soluble in hot alcohol, forms colourless, compact crystals, and is decomposed by alcoholic soda into the sodium salt of the *naphthalido-acid*, which melts at 160 — 161° .

Glycollic α -naphthalide, $C_{12}H_{11}NO_2$, crystallises in colourless, four-sided plates, melts at 126 — 127° , and is insoluble in dilute soda. Tartaric α -naphthalide (compare Abstr., 1895, i, 106), when boiled for some time with acetic anhydride, yields a *tetracetyl* derivative, which crystallises in white needles, and melts at 243 — 244° . Neither the naphthalide nor its acetyl derivative are soluble in caustic soda solution.

J. J. S.

Synthesis of Chrysoketone (Naphthofluorenone) and the Constitution of Chrysene. By CARL GRAEBE (*Ber.*, 1896, 29, 826—828).—The naphthoylbenzoic acid, $C_{10}H_7 \cdot CO \cdot C_6H_4 \cdot COOH$, obtained from naphthalene and phthalic acid, must be an α -naphthalene derivative, for two reasons. First, it yields benzoic acid and α -, but no β -, naphthoic acid when fused with potash; and secondly, it yields an *oxime anhydride*, $C_{10}H_7 \cdot C < \begin{smallmatrix} N-O \\ C_6H_4 \cdot CO \end{smallmatrix}$, melting at 175 — 176° , which, when sublimed, is transformed into α -naphthylphthalimide,

$C_{10}H_7 \cdot N < \begin{smallmatrix} CO \\ CO \end{smallmatrix} > C_6H_4$, melting at 181° , and the latter, when heated with hydrochloric acid at 130° , yields phthalic acid and α -naphthylamine, but no β -naphthylamine. The amide of the acid, $C_{10}H_7 \cdot CO \cdot C_6H_4 \cdot CO \cdot NH_2$, yields a yellow amine, $C_{10}H_7 \cdot CO \cdot C_6H_4 \cdot NH_2$, melting at 140.5° ; when this is diazotised, and the solution then warmed with water, a red substance, $CO < \begin{smallmatrix} C_{10}H_6 \\ C_6H_4 \end{smallmatrix} >$, is formed, identical with the chrysoketone obtained by Bamberger and Kranzfeld from chrysene. It yields a yellow *oxime*, melting at 190° , and is reduced by hydriodic acid and phosphorus to chrysofluorene (which is better called naphthofluorene). All these substances are thus 1:2-naphthalene derivatives, and chrysofluorene has the formula $CH_2 < \begin{smallmatrix} C_{10}H_6 \\ C_6H_4 \end{smallmatrix} >$, chrysene having the formula, $\begin{smallmatrix} CH \cdot C_{10}H_6 \\ || \\ CH \cdot C_6H_4 \end{smallmatrix}$. This proof is held to be better than that deduced from the pyrogenic formation of chrysofluorene (Abstr., 1894, i, 337).
C. F. B.

Acenaphtene [Acenaphthylene] Glycol. By CARL GRAEBE and J. JEQUIER (*Annalen*, 1896, **290**, 205—206).—Ewan and Cohen obtained acenaphthylene glycol by hydrolysing the acetate arising from acenaphthylene bromide (Trans., 1889, 579); a more convenient method of preparation consists in treating the latter with boiling water. A readily soluble modification is produced along with the less soluble form, and melts at 145° ; both are optically inactive, and are probably stereoisomeric.
M. O. F.

Acenaphthenone. By CARL GRAEBE and J. JEQUIER (*Annalen*, 1896, **290**, 195—204).—Acenaphthenone may be prepared from acenaphthene glycol by Ewan and Cohen's method (Trans., 1889, 580), or by reducing acenaphthenequinone (Abstr., 1893, i, 657); the last-named substance, when treated with phosphorus pentachloride, yields *dichloracenaphthenone*, which melts at 146.5° , and gives rise to acenaphthenone when treated with water at 150° . The *picrate* of acenaphthenone crystallises in yellow needles, and melts at 113° ; the *phenylhydrazone* crystallises from alcohol, and melts at 90° . *Bromacenaphthenone* melts at 112° , and yields biacenaphthylidenediketone (*loc. cit.*) when treated with hot dilute caustic soda.

Biacenaphthylidenone (dinaphthylenbutenone), $\begin{smallmatrix} CH_2 \\ | \\ C_{10}H_6 \end{smallmatrix} > C:C < \begin{smallmatrix} CO \\ | \\ C_{10}H_6 \end{smallmatrix}$, is formed from acenaphthenone under the influence of alcoholic potash or acetic chloride, and crystallises from chloroform or benzene in yellow needles, being almost insoluble in alcohol; it melts at 262° (corr.). The ketone combines with two atomic proportions of bromine, yielding the *bromide*, which melts and decomposes at 280° .

Benzylidenacenaphthenone, $C_{10}H_6 < \begin{smallmatrix} C:CHPh \\ CO \end{smallmatrix} >$, is obtained by adding caustic soda to acenaphthenone and benzaldehyde dissolved in alcohol; it melts at 107° , and the *oxime* melts at 48° .
M. O. F.

Orientation in the Terpene Series: Pulegone. By ADOLF VON BAAYER [and BERTRAM PRENTICE] (*Ber.*, 1896, **29**, 1078—1084; compare *Abstr.*, 1895, i, 379).—Nitrosopulegone (*loc. cit.*) is a bis-nitroso-derivative, differing, however, from members of this class in its property of yielding an oxime in addition to a di-nitrosylic acid; this remarkable feature is explained by the fact that the bis-nitroso-group $-\text{NO}_2\text{N}-$, is linked to the methylenic carbon, in juxtaposition to the ketonic group.

Bisnitrosopulegone, $(\text{C}_{10}\text{H}_{15}\text{O})_2\text{N}_2\text{O}_2$, is obtained by adding hydrochloric acid to a mixture of pulegone, light petroleum, and amyl nitrite, cooled with melting ice. Caustic soda converts it into *isonitrosopulegone*, $\text{C}_{10}\text{H}_{15}\text{NO}_2$, which crystallises in straw-yellow needles, and decomposes at $122-127^\circ$; *pulegonedioxime hydrate*, $\text{C}_{10}\text{H}_{18}\text{N}_2\text{O}_3$, is produced by the action of hydroxylamine on isonitrosopulegone.

Pulegonedinitrosylic acid, $\text{C}_{10}\text{H}_{16}\text{N}_2\text{O}_3$, is obtained by the action of hydrogen chloride on an ethereal solution of bisnitrosopulegone; it crystallises from light petroleum in slender, colourless needles, and melts at $115-116^\circ$.

Along with bisnitrosopulegone, there are formed *2-chloropulegone*, which crystallises in long needles, and melts at $124-125^\circ$, and *di-isonitrosomethylcyclohexanone*, the formation of which depends on the elimination of the C_3H_5 group; its empirical formula is $\text{C}_7\text{H}_{10}\text{N}_2\text{O}_3$, and it decomposes at 190° ; the *diacetate* melts at $125-130^\circ$. The *anhydride* of tri-isonitrosomethylcyclohexanone, $\text{C}_7\text{H}_9\text{N}_3\text{O}_2$, obtained by the action of hydroxylamine, melts at $128-129^\circ$; the *acetate* of the anhydride melts at $139-140^\circ$.
M. O. F.

Partial Synthesis of Geranic acid. Constitution of Lemonol [Geraniol] and Lemonaldehyde [Geranaldehyde]. By PHILIPPE BARBIER and LOUIS BOUVEAULT (*Compt. rend.*, 1896, **122**, 393—395).—Since methylheptenonecarboxylic acid and terebic acid are found only in small quantities when lemonaldehyde is oxidised, it seems most probable that they are really derived from impurities. When natural methylheptenone is condensed with ethylic iodoacetate in presence of zinc, and the product is decomposed by water, a colourless oil of the composition $\text{C}_{10}\text{H}_{17}\text{O}_3\text{Et}$ is obtained, which boils at $125-135^\circ$, under a pressure of 7 mm., and yields an acetate which boils at about 140° , under a pressure of 7 mm., and at 250° under ordinary pressure. If the acid $\text{C}_{10}\text{H}_{18}\text{O}_3$ is boiled with acetic anhydride, it is converted into geranic acid, and if the ethereal salt, $\text{C}_{10}\text{H}_{17}\text{O}_3\text{Et}$, or the corresponding acetate, is boiled with acetic acid containing some zinc chloride, ethylic geranate is obtained.

This partial synthesis of geranic acid establishes Tiemann's formula for geranaldehyde, $\text{CHO}\cdot\text{CH}\cdot\text{CMe}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}\cdot\text{CMe}_2$, and necessitates revision of the formulæ proposed by the authors for licareol and licarhodol.
C. H. B.

Extraction of Rhodinol from Oil of Pelargonium and from Oil of Roses. The Identity of these two Products. By PHILIPPE BARBIER and LOUIS BOUVEAULT (*Compt. rend.*, 1896, **122**, 529—531; compare *Abstr.*, 1895, i, 78).—The authors are convinced as to the

difference between rhodinol and geraniol, a difference recently called in question by Erdmann and Huth (this vol., i, 198).

The product extracted from oil of pelargonium contains some geraniol, together with a second alcohol. By treating the extract with benzoic chloride, the geraniol is decomposed, and, on distillation, a benzoate is found in the fraction passing over between 180° and 220° (10 mm.). This, on hydrolysis with alcoholic potash, yields a colourless, agreeably smelling liquid, of the formula $C_{10}H_{20}O$, and boiling at 110° (10 mm.).

For this substance, the authors propose the name rhodinol; its sp gr. = 0.8731 at 0° , and its rotation $\alpha_D = -2^{\circ} 11'$. Its acetate is a colourless, agreeably smelling liquid, boiling at 115° (10 mm.).

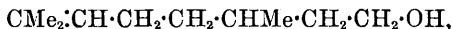
That portion of oil of roses boiling at 110 – 115° (10 mm.), on treatment in the same manner, yields an alcohol having the same boiling point and specific gravity, being also lævorotatory to the same extent. The authors consider the two substances to be identical. Rhodinol occurs in these oils only to the extent of about 20 per cent.

J. F. T.

Constitution of Rhodinol. By PHILIPPE BARBIER and LOUIS BOUVEAULT (*Compt. rend.*, 1896, **122**, 673–675).—Rhodinol (Abstr., 1895, i, 78), when oxidised with chromic mixture, yields (a) *rhodin-aldehyde*, $C_{10}H_{18}O$, which boils at 90° under a pressure of 10 mm., and is under investigation; (b) *rhodinic acid*, $C_9H_{17}\cdot COOH$, an oily liquid, with a powerful and disagreeable odour. It boils at 147° under a pressure of 10 mm., and is identical with the acid obtained by the oxidation of rhodinol from oil of pelargonium, to which the composition $C_{10}H_{16}O_2$ was erroneously attributed (*loc. cit.*); (c) *rhodinylic rhodinate*, $C_{20}H_{36}O_2$, a neutral oil, which has a disagreeable odour, and boils at 190° , under a pressure of 10 mm.

Acetone and β -methyladipic acid are also formed. The acid previously described as α -methyladipic acid (*loc. cit.*) is really the β -modification.

Rhodinol from roses yields similar results, and it follows that rhodinol is a primary open-chain alcohol, with one ethylenic function, and its constitution is most probably



or $CMe_2\cdot CH\cdot CH_2\cdot CHMe\cdot CH_2\cdot CH_2\cdot CH_2\cdot OH$.

C. H. B.

Sobrerol (Δ -Menthene-2 : 8-diol). By ALEXANDER GINZBERG (*Ber.*, 1896, **29**, 1195–1198).—When sobrerol is oxidised by potassium permanganate, the tetrahydric alcohol, *sobreritritol*, $C_{10}H_{20}O_4$, is produced (Wagner, Abstr., 1894, i, 470); this substance is excessively hygroscopic, owing to its tendency to form the *hydrate*, $C_{10}H_{20}O_4 + 2H_2O$, which separates from water in monoclinic crystals, and melts at 100 – 105° , losing water at 120° , after which it melts at 155.5 – 156° . Oxidation of sobreritritol with potassium permanganate yields acetic and terebic acids, the main product being terpenylic acid; from this it follows that the alcohol in question is menthane-

1 : 2 : 6 : 8-tetrol, whilst sobrerol, formed from pinol by rupture of the oxide bond, is Δ^6 -menthene-2 : 8-diol, or Δ^1 -menthene-6 : 8-diol.

Contrary to the statement of Wallach, sobrerol, when treated with boiling acetic anhydride, yields the *diacetate*, a bitter, viscous liquid of agreeable odour, having the sp. gr. = 1.0385 at 18°.

M. O. F.

Dehydration of Menthane-1 : 2 : 8-triol. By ALEXANDER GINZBERG (*Ber.*, 1896, **29**, 1198—1202).—Trihydroxymenthane yields cymene and the *diacetate* of a glycol when heated for six hours with acetic anhydride (3 mols.) at 150°; the *glycol*, $C_{10}H_{18}O_2$, isomeric with sobrerol, separates from light petroleum in colourless, triclinic prisms, melts at 63—64°, and boils at 259—260° under a pressure of 754 mm. Oxidation with potassium permanganate converts it into a tetrahydric *alcohol*, $C_{10}H_{20}O_4$, identical in crystalline form with the limonetrinol of Morosewitz and Wulf; it is, however, optically inactive, and melts at 168.5—169.5°.

The new glycol, which is most probably $\Delta^{8(9)}$ -menthene-1 : 2-diol, is not formed when acetic chloride acts on trihydroxymenthane, the products being sobrerol and cymene.

M. O. F.

Laurolene, a Hydrocarbon of the Camphor Group. By OSSIAN ASCHAN (*Annalen*, 1896, **290**, 185—194).—*Laurolene*, C_8H_{14} , is obtained by slowly distilling camphanic acid in an atmosphere of carbonic anhydride, the yield amounting to 50 per cent. when the operation is conducted at the rate of about 10 drops a minute; if the distillation is carried on more rapidly, a considerable quantity of lauranolic acid is produced (*Abstr.*, 1895, i, 154). *Laurolene* boils at 119° (uncorr.), has the sp. gr. = 0.80187 at 18.6°/4°, and the specific rotatory power $[\alpha]_D = -23.0^\circ$; the refractive index $n_D = 1.4479$ at 18°, whence the molecular refraction $M = 36.70^\circ$, the value calculated for one ethylenic linking being 36.43. The hydrocarbon reduces a cold, alkaline solution of potassium permanganate, and combines with two atomic proportions of bromine; its behaviour towards sulphuric and nitric acids, potassium ferricyanide, and potassium permanganate is inconsistent with the presence of a ring containing 6 atoms of carbon.

M. O. F.

Camphorone, Isophorone, and Mesitylic Oxide. By WILHELM KERP (*Annalen*, 1896, **290**, 123—152).—The author has submitted camphorone to a detailed comparison with phorone obtained by the condensation of acetone, and shows that these substances, although isomeric, are not identical (compare *Abstr.*, 1892, 626); reference is now made to the latter compound as isophorone.

Isophorone, $C_9H_{14}O$, is obtained by the action of sodium ethoxide on acetone, the yield amounting to 7 or 8 per cent.; it boils at 100—102° under a pressure of 15 mm., and the sp. gr. = 0.9255 at 20.5°/4°. When the substance is reduced by adding water to the ethereal solution containing sodium, an *alcohol*, $C_9H_{18}O$, which melts at 37°, and boils at 87° under a pressure of 15 mm., is formed along with the *pinacone*, $C_{18}H_{34}O_2$, which melts at 155°. *Isophoroneoxime* crystallises in transparent prisms, and melts at 79—80°; it is indifferent

towards concentrated sulphuric acid and zinc chloride, and, on reduction with sodium and alcohol, yields the *base* $C_9H_{15}\cdot NH_2$, which boils at $81-85^\circ$, forms the *oxalate* melting at $224-225^\circ$, and the *carbamide* derivative, which crystallises in white needles and melts at 185° . When isophorone is oxidised with potassium permanganate, formic and acetic acids are among the products, also an *acid* of the formula $C_8H_{14}O_4$.

Camphorone, on reduction, yields the *alcohol* $C_9H_{16}O$, which boils at $77-81^\circ$ under a pressure of 16 mm., and the *pinacone* $C_{18}H_{30}O_2$, which sinters at $135-140^\circ$, and melts at $160-162^\circ$. Camphorone-oxime (Abstr., 1893, i, 361) contains $1H_2O$, and, on reduction, yields a base which probably has the formula $OH\cdot C_9H_{16}\cdot NH_2$; the *oxalate* is crystalline.

Camphorone, isophorone, and crystallised acetophorone all yield pseudocumene when they are distilled with phosphoric anhydride; the first-named also gives rise to cumene, whilst acetophorone yields mesitylene.

Reduction of mesitylic oxide converts it into methylisobutyl-carbinol. The oxime yields β -isohexylamine and hydroxy- β -isohexylamine.

β -Isohexylamine, $C_6H_{15}N$, is a limpid base of ammoniacal odour which absorbs atmospheric carbonic anhydride, and boils at $100-103^\circ$; the *hydrochloride* and *platinochloride* are well defined, the *oxalate* melts at 219° , and the *carbamide* derivative at $139.5-140^\circ$.

Hydroxy- β -isohexylamine, $OH\cdot C_6H_{12}\cdot NH_2$, has a feebly ammoniacal odour, and boils at $171-174^\circ$; the *oxalate* melts at 206° .

The *hydrocarbon* C_6H_{10} is produced along with the foregoing bases, and boils at $77-78^\circ$; the *tribromo-compound*, $C_6H_9Br_3$, is an oil.

M. O. F.

Conversion of Dextrocamphoric acid into Dextrocamphor.

By ALBIN HALLER (*Compt. rend.*, 1896, 122, 446-449).—When campholide is heated with potassium cyanide in sealed tubes at $230-240^\circ$, it yields cyanocampholic acid, identical with that obtained from cyanocamphor, and this acid, when heated with potassium hydroxide, yields bromocamphoric acid, identical with that prepared from cyanocamphor. The lead salt of this bromocamphoric acid, when heated, yields camphor identical in all its properties with ordinary camphor.

These results show (1) which part of the molecule is oxidised in the conversion of camphor into camphoric acid, (2) that the fundamental nucleus to which camphor owes its rotatory power is not destroyed by conversion into camphoric acid, campholide, cyanocampholic acid, or bromocamphoric acid. They are also in accordance with the view that the camphoric and bromocamphoric acids have a double carboxylic function.

C. H. B.

Russian Oil of Anise. By GUSTAVE BOUCHARDAT and TARDY (*Compt. rend.*, 1896, 122, 624-626).—The commercial oil contains a large proportion of anethoil, $C_{20}H_{32}O_3$, a very small quantity of anisaldehyde, anisic acetone, $C_{20}H_{30}O_4$, anisic acid, and anethoil,

fenchone, $C_{20}H_{16}O_2$, and also some hydrocarbons of the formula $C_{30}H_{24}$.
No new compounds are described in this paper. J. F. T.

Euxanthone. By F. MANN and BERNHARD TOLLENS (*Annalen*, 1896, **290**, 159—164).—The *disodium* and *dipotassium* derivatives are crystalline, and the *calcium* derivative is obtained as a gelatinous precipitate on adding a solution of calcium chloride to euxanthone dissolved in ammonia and alcohol; the *barium* derivative separates from dilute alcohol in red crystals.

When euxanthone is reduced with sodium amalgam, the compound $C_{26}H_{18}O_7$ is obtained, separating from alcohol in dark violet crusts; the solution in concentrated hydrochloric acid is red, the absorption spectrum exhibiting a band almost coincident with the D line.

M. O. F.

Isatin. By LEO MARCHLEWSKI (*Ber.*, 1896, **29**, 1030—1034).—Isatin readily reacts with semicarbazide to form a *semicarbazone*, $N \leq \overset{C_6H_4}{C(OH)} > C:N \cdot NH \cdot CO \cdot NH_2$, which crystallises in yellow needles, melts and decomposes at about 260° , and dissolves in strong aqueous soda and strong acids, but not in dilute acids. *Parachlorisatinsemicarbazone* crystallises in stellate groups of light yellow needles, and is more strongly acid than isatinsemicarbazone. It becomes brown at about 230° . *Nitroisatinsemicarbazone* crystallises in slender, pale yellow needles. Isatin and its derivatives, therefore, act as monoketones towards semicarbazide. A. H.

Carbostyryl and its Derivatives: Tautomerism. By ADOLPH CLAUS (*J. pr. Chem.*, 1896, [2], **53**, 325—334).—The bromination of carbostyryl leads to the conclusion that it exists in tautomeric forms, and the author develops the theory which he has previously outlined (*Abstr.*, 1895, i, 257) in this connection. The subject of tautomerism must now be considered from three points of view, namely, that of the “central” linking theory (*loc. cit.*), that of the existence of racemic forms, and that of continually changing bonds.

A. G. B.

4-Hydroxyquinoline. By ADOLPH CLAUS (*J. pr. Chem.*, 1896, [2], **53**, 335—339; compare *Abstr.*, 1893, i, 484; this vol., i, 255).—When 4-hydroxyquinoline and bromine, in molecular proportion, are brought together in glacial acetic acid, a yellow, crystalline precipitate is formed, consisting of a mixture of the hydrobromides of 4-hydroxyquinoline, 1 : 4-bromohydroxyquinoline, and 1 : 3 : 4-dibromohydroxyquinoline. To separate these, the aqueous solution of the precipitate is much diluted, whereby the dibromo-derivative, being a very feeble base, is thrown down; the bromo-derivative may then be precipitated by the addition of sodium acetate.

1 : 4-*Bromohydroxyquinoline* darkens at 165 — 170° , and melts at about 190° . 1 : 3 : 4-*Dibromohydroxyquinoline* begins to decompose at 130 — 140° , and does not melt at 300° .

3 : 4-*Bromohydroxyquinoline* crystallises in yellowish needles, and melts at 162° .

4 : 1-*Hydroxyquinolinesulphonic acid* is obtained by sulphonating 4-hydroxyquinoline in the usual manner; it crystallises, when hydrochloric acid is added to the hot solution of its sodium salt, in lustrous, yellow prisms, with $1\text{H}_2\text{O}$, and melts at about 300° ; it is only very slightly soluble in neutral solvents; its *sodium* salt forms hard, brilliant, dark red prisms with $1\text{H}_2\text{O}$.
A. G. B.

Reactions of Salts of Alkaloids with various Indicators. By H. W. SALOMONSON (*Chem. Centr.*, 1895, ii, 536, 826; from *Ned. Tydschr. Pharm.*, 7, 195—203; 225—234).—The author has found that quinine is a dibasic alkaloid, and that the compound of 1 mol. of quinine with 2 mols. of hydrogen chloride must therefore be considered as the normal salt. If this salt were of an acid nature, it would not be neutral to methyl-orange; it is, however, acid to litmus.

When titrating salts of quinine, good results are obtained by the use (1) of indicators which are not acted on by the liberated alkaloid until the last trace of acid has been neutralised; for example, phenolphthaleïn; (2) of indicators such as rosolic acid, and litmus, which are affected not by the free alkaloid, but by its basic salts; (3) of indicators such as methyl-orange, which are only dissociated by perfectly neutral salts.
L. DE K.

Isolation of Adenine from Tea Extract. By MARTIN KRÜGER (*Zeit. Physiol. Chem.*, 1895, 21, 4, 274—284).—Of the methods for isolating adenine (1) by ammoniacal silver nitrate, and (2) by copper sulphate and sodium hydrogen sulphite, direct comparison shows the latter to be the better.

The adenine precipitated by the former method is accompanied by a second substance which may be obtained from the mother liquors. It crystallises in delicate, silky prisms, and dissolves readily in hot water, less readily in cold. From its aqueous solution, picric acid precipitates adenine picrate, whilst theobromine occurs in the mother liquor. The substance is, therefore, a compound of adenine and theobromine, $\text{C}_5\text{H}_5\text{N}, \text{C}_7\text{H}_7\text{N}_4\text{O}_2$, and may be obtained by dissolving molecular proportions of its constituents in hot water, when it separates in delicate white needles. On recrystallisation from water, it is decomposed, theobromine being deposited.

A third substance occurring in the above silver precipitate is isolated after precipitating the adenine by means of picric acid from the mixture of free bases. The mother liquors are freed from picric acid by acidification and extraction with ether, the bases being then precipitated by ammoniacal silver nitrate. The precipitate is recrystallised from dilute nitric acid, the less soluble portions being collected and decomposed in hot water by hydrogen sulphide, the filtered liquid being then boiled and rendered alkaline by ammonia. The new base is precipitated in aggregates of long, slender, needles, and dissolves somewhat readily in hot water; on treatment with concentrated nitric acid, a dark yellow substance is left which becomes a brilliant red with gaseous ammonia or sodium hydroxide; when acted on by a mixture of hydrochloric acid and potassium chlorate, and then with gaseous ammonia, a violet-red coloration is produced. It

dissolves in 33 per cent. caustic soda, and, with picric acid, gives yellow needles soluble in water. The *hydrochloride* is sparingly soluble in hydrochloric acid, and forms shining, colourless needles; the *nitrate* forms compact, faceted, lustrous crystals; the *platino-chloride* crystallises in brilliant, four-sided, orange-red prisms, and the *aurochloride* in fern-like, skeleton forms.

Hypoxanthine does not occur in tea extract, but is probably produced from the silver derivative of adenine by the oxidising action of the nitric acid from which it is usually crystallised, hence the statements as to its presence. A. L.

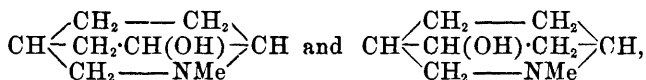
Pseudaconitine. By MARTIN FREUND and ROBERT NIEDERHOFHEIM (*Ber.*, 1896, 29, 852—858).—The pseudaconitine investigated by the authors melted at 212° , whilst the melting point is stated to be $104\text{--}105^{\circ}$ by Wright (*Trans.*, 1878, 151), and 201° by Dunstan and Carr (*Proc.*, 1895, 154). The *hydriodide*, $\text{C}_{38}\text{H}_{49}\text{NO}_{12}\cdot\text{HI}$, crystallises in prisms, and melts at $215\text{--}217^{\circ}$. The *aurochloride* melts at $236\text{--}238^{\circ}$, whilst the *nitrate* crystallises in thin prisms or plates which melt and decompose at $185\text{--}186^{\circ}$, and the *thiocyanate* decomposes at $195\text{--}200^{\circ}$.

When the base is boiled with water, it yields acetic acid and *picropseudaconitine*, $\text{C}_{34}\text{H}_{47}\text{NO}_{11}$, which forms compact crystals melting at 210° ; a fact previously established by Dunstan and Carr (*loc. cit.*), who, however, give the m. p. as 181° . The *hydriodide* crystallises in prisms which melt and decompose at $205\text{--}207^{\circ}$. No crystalline nitrate could be obtained. When picropseudaconitine is boiled with strong aqueous potash, it yields veratric acid and *pseudaconine*, $\text{C}_{25}\text{H}_{39}\text{NO}_8$, to which Wright gave the formula $\text{C}_{27}\text{H}_{41}\text{NO}_8$. It is a yellowish-brown, amorphous mass, but yields a crystalline *acetone compound*, $\text{C}_{25}\text{H}_{39}\text{NO}_8 + \text{C}_3\text{H}_6\text{O}$, which melts at $86\text{--}87^{\circ}$, and dissolves in water, forming a solution which leaves the amorphous pseudaconine when evaporated. It crystallises in hemihedral forms of the rhombic system, the crystallographic constants being $a : b : c = 0.95462 : 1 : 1.3735$.

These results make it probable that pseudaconitine is acetylveratroylanhydro-aconine, $\text{C}_6\text{H}_5(\text{OMe})_2\cdot\text{CO}\cdot\text{C}_{25}\text{H}_{37}\text{NO}_8\cdot\text{Ac}$. A. H.

Note.—Most of the facts in the above paper have been already published by Dunstan and Carr in a preliminary communication to this Society (*Proc.*, 1895, 154), in which they stated that they were still engaged in this investigation.—EDITORS.

Ketones of the Tropine-group II.— ψ -Tropine. By RICHARD WILLSTÄTTER (*Ber.*, 1896, 29, 936—947).—The preparation of tropinone from tropine has been previously described (this vol., i, 327). When reduced by means of sodium in moist ethereal or alcoholic solution, or by sodium amalgam in dilute hydrochloric acid solution, tropinone is converted into ψ -tropine, which was fully identified by the preparation of numerous derivatives; when oxidised, tropinone is regenerated. Tropine is readily converted into ψ -tropine by heating with sodium amyloxide in amylic alcoholic solution; these results show that the compounds are not structurally isomeric,



as Liebermann suggested. Both are optically inactive, and contain three asymmetric carbon atoms (see below); three cases of geometrical isomerism are discussed.

(1) *Isomerism of Cyclohexane*.—Sachse (Abstr., 1890, 1386) has shown that cyclohexane and its derivatives might exist in two forms, but no experimental verification of this has been given, and no isomeric hexahydrobenzoic acid is known; v. Baeyer's present view is that the carbon atoms in cyclohexane, as in the other polymethylenes, are in one plane, and that the cause of *cis-trans*-isomerism lies in their occupying a middle position of greatest stability.

(2) *Isomerism as in the case of Piperidine Derivatives*.—This has been discussed by Ladenburg (Abstr., 1893, i, 442; and 1894, i, 306), but lacks experimental proof.

(3) *Isomerism due to the Double Ring containing Nitrogen*.—Until the geometrical isomerism occurring in double ring compounds, such as borneol derivatives, and in cyclic nitrogen compounds, such as the monosubstitution products of piperidine, has been fully investigated, the discussion of this form of geometrical isomerism would be premature.

The author inclines to the belief that the relationship of tropine and ψ -tropine is an instance of *cis-trans*-isomerism due to the relative position in space of the methyl and hydroxyl groups.

Ladenburg has suggested (*Ber.*, 1896, 29, 424) that tropinone is an aldehyde, and has pointed out that its production accords as well with his as with Merling's tropine formula. The subject is being further investigated, but the production of tropinic acid from dihydroxytropidine, and its resolution into adipic acid is against Ladenburg's view.

Tropinone is very readily reduced by sodium in boiling alcoholic solution, or by means of sodium amalgam (see above); the yield of ψ -tropine is quantitative, and no tropine could be detected, even traces. *Benzoyl- ψ -tropeine*, prepared by Liebermann's method from ψ -tropine, is identical with tropacocaine contained in Java coca leaves, and is the first example of the conversion of an alkaloïd of the Solanaceæ into one of the Erythroxylæ (coca), and it affords confirmation of the relationship which has been shown to exist between the cocaine and atropine groups. The *nitrate* and *picrate* are sparingly soluble; the *hydrobromide* crystallises in silky, lustrous plates; the *hydrochloride* in highly refractive, rhombic plates melting and decomposing at 270°. The *mercurochloride* is crystalline; the *platinochloride* is deposited in pale, slender needles; the *aurochloride* crystallises in needles melting and decomposing at 207–208°. The yield of ψ -tropine, boiling within three degrees, prepared directly from tropine, is 75 per cent. of the theoretical, that of the purified product is 50–55 per cent. Attempts to regenerate tropine from ψ -tropine by the action of sulphuric acid at the ordinary temperature were unsuccessful.

J. B. T.

A New Enzyme from Yeast. By A. BAU (*Chem. Zeit.*, 1895, 19, 1873—1874).—Melitriose, when treated with an invertase solution, is hydrolysed to melibiose and a monose (probably fructose), both of which the author has isolated in the form of their osazones. It is stated that yeast, dried at such a temperature as not to destroy the enzymes, and then digested with water, yields no sugar, whereas Salkowski states that fresh yeast when digested with water yields fructose.

A melibiose solution when digested with dried top yeast is not acted on, but with dried bottom yeast (Frohberg type) it is completely converted into glucose and galactose. A mixture of the two yeasts also brings about the same decomposition. The enzyme which is present in the bottom yeast and which brings about this decomposition, the author terms *melibiase*.

Thus in yeast (so-called *Saccharomyces cerevisiæ*) the following enzymes are present: (1) Invertase, or, as the author prefers to term it, *eninvertase*, this is soluble in water, is precipitated by alcohol and decomposes cane sugar into glucose and fructose, and melitriose into fructose and melibiose; (2) yeast glucase (compare C. J. Lintner and Emil Fischer), which is insoluble in water, and which decomposes maltose and isomaltose into glucose; (3) melibiase, also insoluble in water.

J. J. S.

Constitution of Cholic acid. By MICHAEL SEŃKOWSKI (*Monatsh.*, 1896, 17, 1—3).—Cholic acid behaves towards halogens as a saturated compound. It is oxidised by alkaline permanganate, the resulting mixture of acids yielding, on distillation with steam, acetic and propionic acids but no benzoic acid; the non-volatile portion when extracted with ether, yields some impure phthalic acid.

A. L.

Specific Rotation of Cholic acid, Choleic acid, and Deoxycholic acid. By E. VAHLEN (*Zeit. physiol. Chem.*, 1895, 21, 4, 253—273).—Cholic acid is most readily purified by preparing its potassium salt, dissolving the latter in dilute alcohol, and precipitating it with a mixture of absolute alcohol and ether, the crystalline precipitate being washed with the same mixture; the last traces of colouring matter may be removed by exposing the acid to sunlight. Crystals of the acid from acetic acid and hot alcohol melt at 180—187° (not 185—187°).

Determinations of the rotatory power of cholic acid made (1) with specimens containing 1 mol. of alcohol of crystallisation, gave $[\alpha]_D = 35.11$; (2) with specimens of pure acid, gave $[\alpha]_D = 37.02$. The high value $[\alpha]_D = 49.4$ obtained by Hoppe Seyler (*J. pr. Chem.*, 1863, 2, 257) from direct observation on solutions of the dry acid were certainly due to impurity. Potassium cholate in aqueous solution gave values of $[\alpha]_D = 26.66$ —31.35, whence the deduced values for free cholic acid are $[\alpha]_D = 29.22$ —34.35; in alcoholic solution the salt has the rotation $[\alpha]_D = 31.27$ —31.59, whence for free cholic acid, $[\alpha]_D = 34.26$. Sodium cholate in aqueous solution gave numbers making $[\alpha]_D = 27.45$ —30.61, giving for free cholic acid

$[\alpha]_D = 29.03-32.37$. The mean molecular rotations of the potassium and sodium salts are practically identical.

Dextrorotatory choleic acid in aqueous solution has a specific rotation $[\alpha]_D = +48.60-52.48$.

The rotations of the above substances were found to be considerably affected by the concentration and temperature of the solutions.

Deoxycholic acid, prepared according to Mylius's directions from putrefying ox-gall, melted at $153-155^\circ$ (not $160-170^\circ$), and had in alcoholic solution the specific rotation $[\alpha]_D = +49.86$. A. L.

Proteïds of the Kidney Bean (*Phaseolus Vulgaris*). By THOMAS B. OSBORNE (*J. Amer. Chem. Soc.*, 1894, **16**, 633-643 and 703-712).—The author confirms most of the work previously done by Ritthausen (*J. pr. Chem.*, **103**, 204, and [2], **29**, 452), but states that the aqueous extract of the bean is always distinctly acid, and also, in opposition to Ritthausen, that a 5 per cent. saline solution extracts a proteïd from the crushed beans.

The author has been enabled to identify and obtain in a state of comparative purity two distinct proteïds, one, the more abundant, having the properties of a globulin, which he designates *phaseolin*, and another, not so definite in character, which he terms *phaselin*.

The phaseolin is best obtained by extracting freshly ground bean meal, which has been treated with ether, with sodium chloride solutions (1-10 per cent.), and then precipitating with water, ammonium sulphate, or dilute acids. The precipitate, after filtration for 24 hours, and after dialysis for about six days in river water, consists of nearly pure phaseolin. That it really consists of a single proteïd has been shown by repeated fractional precipitation; each fraction was found to give practically the same results, on analysis. The amount of proteïd extracted by a sodium chloride solution is about 15 per cent. of the seed. Water is found to extract about 11 per cent. of the same proteïd. The phaseolin was obtained in the form of well-formed tetrahedral crystals by taking the clear extract obtained by a 1 per cent. sodium chloride solution and dialysing in a large vessel containing alcohol. The analysis of the purest sample obtained by repeated solution and precipitation gave C = 52.49, H = 6.90, N = 16.46, S = 0.50, ash = 0.69.

It is entirely insoluble in cold or warm distilled water, but readily dissolves in sodium chloride solution and in very dilute acids and alkalis, yielding a clear solution. Acetic, hydrochloric, nitric, and sulphuric acids do not precipitate the proteïd from its 10 per cent. sodium chloride solution, but it is precipitated from its 1 per cent. sodium chloride solution by means of dilute hydrochloric acid. Solutions of the proteïd in brine are all precipitated by ammonium sulphate, or by a mixture of potassium ferrocyanide and acetic acid.

A violet colour is obtained with copper sulphate and potash, and with nitric acid, the xanthoproteïc reaction is given.

No turbidity occurs in the 2 per cent. sodium chloride solution until the temperature reaches 95° , and at 100° , a small quantity of a flocculent precipitate is formed. In composition, it resembles the myosins found in maize and oats (Abstr., 1891, 1390).

The second proteïd, *phaseolin*, remains in solution after the phaseolin has been precipitated, and may be separated by dialysis in distilled water, by adding acids, and by prolonged heating. The proteïd obtained by any of these means has nearly the same composition. The purest specimen gave C = 49.01, H = 6.77, N = 14.04, ash = 4.58 per cent. When dried over sulphuric acid, it is almost wholly soluble in water, but, after drying at 110°, it becomes insoluble.

J. J. S.

The Proteïds of Barley. By THOMAS B. OSBORNE (*J. Amer. Chem. Soc.*, 1895, 17, 539—567).—The proteïds, which are soluble in water, the author shows to be leucosin and proteose (compare this vol., i, 399), and the proteïd soluble in sodium chloride solution is edestin (this vol., i, 400). Another proteïd, however, occurs in barley meal; this is soluble in dilute alcohol (75 per cent.), and the author designates it *hordein*. This hordein is apparently the same proteïd as that described by Kreusler; it resembles gliadin in many of its properties, but differs from it considerably in composition; hordein contains $1\frac{1}{2}$ per cent. more carbon, $1\frac{1}{2}$ per cent. less nitrogen, and 0.3 per cent. less sulphur than gliadin. When completely dried at 110°, hordein is almost insoluble in water; the dilute solutions, which can be obtained by means of hot water, do not precipitate on cooling, or coagulate on boiling, but yield a precipitate on the addition of salt. It is also soluble in very dilute alkalis and acids, but is thrown down again on neutralisation. Dissolved in concentrated hydrochloric acid, a beautiful, crimson colour is produced, and a warm mixture of equal volumes of water and concentrated sulphuric acid gives a red colour with hordein, not a purple-red, as with gliadin.

Barley also contains a proteïd, insoluble in water, saline solutions, and alcohol, but soluble in potash. It was not found possible to isolate this compound in a state of purity.

The amounts of the various proteïds present are, globulin (estedin) and proteose, 1.95 per cent.; leucosin, 0.3 per cent.; hordein, 4 per cent.; and insoluble proteïd, 4.5 per cent.

J. J. S.

Deamidation of Glutin-Peptide. By CARL PAAL (*Ber.*, 1896, 29, 1084—1085; compare Abstr., 1894, 559).—When nitrous acid acts on gluten-peptide, nitrogen is eliminated, and a nitrosamine is produced; this indicates the existence of an imido-group along with amido-nitrogen in the original substance, which also contains tertiary nitrogen, because the nitrosamine in question has basic properties.

Deamidonitrosogluten-peptide is obtained by carefully adding silver nitrite suspended in water to a solution of gluten-peptide hydrochloride in hot water, the operation being finished when dissolved silver appears in the liquid; silver chloride having been removed by filtration, the solution is treated with hydrogen sulphide until nitrous acid is no longer present, filtered from silver sulphide, and extracted with ether in order to remove an oily by-product. The aqueous solution is then evaporated, and the residual syrup poured into absolute alcohol, which precipitates the amorphous peptide derivative; the alcoholic solution deposits it as a yellow, brittle, vesicular

mass, which is very hygroscopic, and dissolves most readily in water, being sparingly soluble in hot, absolute methylic alcohol. The substance gives the biuret reaction, and is precipitated by phosphotungstic acid in alkaline or acid solution; concentrated sulphuric acid eliminates the nitroso-group in the form of nitrous acid.

When treated with much ether, the filtrate from the precipitate of deamidonitrosopeptone obtained on pouring the aqueous syrup into absolute alcohol, yields a substance which the author calls *deamidonitrosopeptone*, giving the biuret reaction, and being precipitated by phosphotungstic acid. These two new compounds have been obtained from three distinct preparations of gluten-peptone, and details are given regarding the production and properties of their *hydrochlorides*.

Deamidogluten-peptone is formed from deamidonitrosopeptone on eliminating the nitroso-group by reduction with zinc and dilute sulphuric acid; it is thus obtained as a pale yellow, hygroscopic mass, which dissolves sparingly in hot ethylic alcohol. The substance gives the biuret reaction, and is precipitated by phosphotungstic acid. The *hydrochloride* is a yellow, hygroscopic mass. M. O. F.

Mucin of Connective Tissue. By RUSSELL H. CHITTENDEN and WILLIAM J. GIES (*J. Exper. Med.*, 1896, 1, 188—201).—Mucin prepared from tendons by precipitating the lime water extract of them with hydrochloric acid, gave the following percentages on elementary analysis.

	1.	2.	3.	Loebisch's average (Abstr., 1886, 166).
C	49.29	48.74	48.26	48.30
H	6.63	6.46	6.49	6.44
N	11.94	11.80	11.51	11.75
S	2.34	2.35	2.31	0.81
O	29.80	30.65	31.43	32.70

No. 3 is regarded as the purest preparation and the results agree closely with those of Loebisch, except in the percentage of sulphur. There is, however, probably more than one mucin in connective tissue, and the sulphur may be largely due to admixture with proteid matter. Preliminary extraction of the tissue with 10 per cent. sodium chloride solution is the best way to get rid of this. This was done in the case of preparation 3.

The reactions of mucin are well given by Loebisch. From the carbohydrate which can be cleaved off from it, a crystalline osazone was prepared, melting at 160°. It appears to resemble very closely that obtained by Hammarsten from the nucleo-proteid of the pancreas (Abstr., 1894, i, 310). W. D. H.

Organic Chemistry.

Conversion of Trimethylene into Propylene. By SIMEON M. TANATAR (*Ber.*, 1896, **29**, 1297—1300).—When trimethylene is passed slowly through a glass tube heated to a dull red heat in a combustion furnace, the product is absorbed, for the most part, by cooled sulphuric acid, and from the resulting solution isopropyllic (and propyllic) alcohols can be isolated. A conversion of trimethylene into its isomeride, propylene, must have taken place in the tube; this corresponds with a loss of energy (7·7 Calories), and is analogous to the conversion of maleic into fumaric acid. C. F. B.

Preparation of Diethylenic Hydrocarbons. By H. FOURNIER (*Bull. Soc. Chim.*, 1895, [3], **13**, 882—884).—The author describes certain hydrocarbons produced by the elimination of the elements of water from the secondary alcohols previously described by him (*Abstr.*, 1894, i, 19, 394; 1895, i, 198). The alcohol is heated in an oil bath at 120°, with three times its weight of potassium hydrogen sulphate for some time. The hydrocarbon is then distilled over, and purified by fractionation.

Methyl-6-heptandiene-1 : 3, $\text{CHMe}_2\cdot\text{CH}_2\cdot\text{CH}:\text{CH}:\text{CH}:\text{CH}_2$, is prepared from isobutylallylcarbinol; it boils at 115—117°, and its sp. gr. = 0·741 at 22°.

Decandiene-1 : 3, $\text{C}_8\text{H}_{13}\cdot\text{CH}:\text{CH}:\text{CH}:\text{CH}_2$?, is formed from hexylallylcarbinol. It is a colourless liquid boiling at 168—170°, and having a sp. gr. = 0·750 at 20°. J. F. T.

Preparation of Allylene [Methylacetylene]. By EDWARD H. KEISER (*Amer. Chem. J.*, 1896, **18**, 328—332; compare Keiser and Breid, *Abstr.*, 1895, 405).—The product of the interaction of alcohols and red-hot magnesium readily evolves a mixture of hydrogen and allylene when placed in water, best containing a little ammonium chloride; the allylene and hydrogen are readily separated by passing the mixture through ammoniacal silver nitrate solution, when silver allylide is precipitated. The maximum yield of the hydrocarbon is obtained with acetone and magnesium; the usual method of preparation is to heat the magnesium in thin-walled iron tubes, closed with an asbestos stopper pierced with holes which serve to admit two glass tubes; through one of these acetone vapour is admitted, whilst gaseous products formed during the action escape through the other. The solid black mass thus produced affords a considerable quantity of allylene when treated in the above manner.

Analyses of the gases, evolved when these products are treated with water, show that they are mixtures of hydrocarbons with free hydrogen; the absence of oxides of carbon leads the author to suppose that a portion of the magnesium combines with the oxygen of the alcohol, the hydrocarbons thus produced combining with a second portion of the magnesium to form magnesium allylide. That

the latter substance is present in the black mass appears certain from a consideration of the behaviour of the latter with water, and of the fact that it contains hydrogen; further, when magnesium is burned in oxides of carbon, the residue evolves only minute traces of allylene when treated with water.

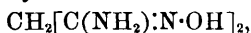
The silver and copper precipitates formed on passing the mixed gases into water, appear to be the pure allylides, as, on analysis, they gave numbers agreeing closely with those required for AgC_3H_3 and CuC_3H_3 ; the mercury precipitate crystallised from alcohol, and showed the properties of mercury allylide. From determinations of the content of hydrogen in the magnesium residue and of the amount of silver allylide obtained from acetone, it appears that the yield is about one-tenth of that indicated by the equation



The author is investigating the properties of allylene, and finds that the gas is readily absorbed by sulphuric acid; the product, probably a sulphonic acid, yielding a crystalline barium salt.

A. L.

Derivatives of Malononitrile. By HERMANN SCHMIDTMANN (*Ber.*, 1896, **29**, 1168—1175).—Malononitrile, $\text{CH}_2(\text{CN})_2$ (1 mol.), when treated with hydroxylamine (1 mol.) yields *cyanethenylamidoxime*, $\text{CN}\cdot\text{CH}_2\cdot\text{C}(\text{NH}_2)\cdot\text{N}\cdot\text{OH}$, a rather unstable substance, which melts and decomposes at 124—127°, and yields *acetyl* and *benzoyl derivatives* melting respectively at 142°, and at 184—192° (with decomposition). When treated with double the quantity of hydroxylamine, malononitrile yields *malonenediamidoxime*,



which melts and decomposes at 163—167°; the *diacetyl* and *dibenzoyl derivatives* melt and decompose at 153—159° and 183—185°, and, by prolonged heating at 160° or by boiling with 10 per cent. caustic soda, are converted, respectively into *malonenediazoximedienyl*, $\text{CH}_2(\text{C} \begin{smallmatrix} \text{N} \\ \text{NO} \end{smallmatrix} \text{CMe})_2$, which softens at 92° and melts at 99°, and *malonenediazoximedibenzenyl*, which melts at 175°.

When malononitrile (1 mol.) is treated with alcoholic sodium ethoxide (1 mol.), a sodium salt, $\text{CHNa}(\text{CN})_2$, is formed. If this is treated with 2 mols. of sodium ethoxide, and cyanogen chloride is passed into the solution, *sodiocyanoforn*, $\text{CNa}(\text{CN})_3$, is formed in amount equal to 70 per cent. of the theoretical; *silver cyanoforn* was also prepared and analysed. When the sodium compound is treated with dilute sulphuric acid, nothing separates, but if the whole is now shaken with ether, a separation into three layers ensues, of which the middle layer appears to be cyanoforn, the uppermost an ethereal solution of it. *Cyanoforn*, $\text{CH}(\text{CN})_3$, was obtained as a greenish liquid which, when concentrated in a vacuum beyond a certain point, formed a mass of brownish crystals (polymerisation?). It crystallises with 1 mol. of methylic or of ethylic alcohol, but the alcohol is not to be regarded simply as alcohol of crystallisation, for these compounds can be crystallised from water without undergoing any

change; they soften and turn yellow at 205° and 215° respectively, and finally melt and decompose at $214\text{--}215^{\circ}$ and $219\text{--}220^{\circ}$. It was not found possible, by the action of cyanogen chloride on the sodium derivative, to displace the hydrogen atom in cyanoform by the cyano-gen group.

Malononitrile (1 mol.), when dissolved in ice-cold aqueous caustic potash (1 mol.), condenses with diazobenzene nitrate, forming *phenylhydrazonemesoxalonitrile*, $\text{NHP}h\cdot\text{N}:\text{C}(\text{CN})_2$, a yellow substance which melts and decomposes at $130\text{--}144^{\circ}$, dissolves in caustic alkalis but not in alkali carbonates or in acids, and dyes wool yellow.

C. F. B.

Preparation of Mannose. By DUYVENÉ DE WITT (*Chem. Centr.*, 1895, ii, 862—863; from *Zeit. Ver. Rübenzuck-Ind.*, 1895, 794—795).—The author recommends the decomposition of the phenylhydrazone of mannose by means of benzaldehyde as a means of obtaining mannose. 1 kilo. of ivory-nut turnings was heated with 2 litres of 6 per cent. hydrochloric acid for six hours, filtered, washed with hot water, the acid solution neutralised with solid sodium carbonate, again filtered, and decolorised with animal charcoal. The requisite quantity of phenylhydrazine hydrochloride and an excess of sodium acetate, dissolved in water, were added, and the crystals thus obtained were heated for two hours with a mixture of benzaldehyde, alcohol, and water, and then filtered. The filtrate, on evaporation in a vacuum, gave a syrup which contained 89.6 per cent. of mannose.

J. J. S.

Preparation of Glycerose. By FONZES-DIACON (*Bull. Soc. Chim.*, 1895, [3], 13, 862—863).—On heating a mixture of anhydrous glycerol and mercuric chloride to 160° , a very energetic action ensues, mercurous chloride being precipitated in large quantity; by prolonging the action, the mercurous chloride itself is completely reduced, and the product obtained on neutralising with sodium carbonate and filtering, is a yellow liquid showing strong reducing properties.

The *osazone* of this compound is readily purified by dissolving it in alcohol and reprecipitating with water. It is a slightly coloured crystalline powder, insoluble in cold water, and melting at 131° , which is the melting point of phenylglycerosazone obtained by Fischer and Tafel (*Abstr.*, 1887, 651) from glycerose.

J. F. T.

Levulose and Humous Substances derived from it. By BOHUSLAV RÁYMAN and OTTOKAR ŠULC (*Chem. Centr.*, 1895, ii, 593).—Aqueous solutions of pure levulose, when heated to $100\text{--}120^{\circ}$, are readily decomposed, an odour of caramel is developed, and humous compounds are formed; the decomposition could not be followed quantitatively by the measure of the rotary or of the reducing power of the solutions. The filtered solution, on distillation with steam, gave a distillate containing furfuraldehyde, formic acid, and formaldehyde, whilst the residue, on evaporation, deposited flocculent humous substances, formed by the decomposition of an acid, $\text{C}_6\text{H}_8\text{O}_6$, which the authors have isolated in the form of its calcium salt, and term *pyrolevulinic acid*. This acid reduces Fehling's solution, and

also silver, bismuth, and mercury salts, the metals being deposited. Its reducing power on Fehling's solution is 2.9 times weaker than that of levulose. The analysis of the humous substance indicates the composition $C_{25}H_{22}O_{10}$.

The authors are making experiments to determine whether the decomposition of levulose can be followed quantitatively by estimating the amount of formic acid produced. When treated with dilute sulphuric acid, pyrolevulinic acid is decomposed into carbonic anhydride and an acid probably identical with levulinic acid. J. J. S.

Nitrogen Pentethyl. By ARTHUR LACHMAN (*Amer. Chem. J.*, 1896, **18**, 372—375).—In the hope of preparing the compound $N(C_2H_5)_5$, the author studied the action of zinc ethyl on tetrethylammonium iodide. After a mixture of the two substances dissolved in ether had remained for from four to six weeks, it was poured into water whereon an alkaline solution [indicator not given] was obtained which turned yellow, and deposited a finely crystalline, red precipitate, apparently tetrethylammonium tri-iodide. This reaction has not been explained.

The reaction between zinc ethyl and triethylamine dibromide produces triethylamine, ethylic bromide, and zinc ethobromide; no evidence of nitrogen pentethyl was obtained. Phenylic iodochloride reacts with zinc ethide to form phenylic iodide, ethylic chloride, and zinc chloride and oxychloride. A. G. B.

The Action of Acid Chlorides on the Salts of the Nitro-paraffins. By JOHN U. NEF and L. W. JONES (*Ber.*, 1896, **29**, 1218—1224).—When benzoic chloride acts on sodium nitroethane, either dissolved in water or suspended in ether, several products are formed. That portion which dissolves in sodium hydrogen carbonate solution consists of *benzoylacethydroxamic acid*, $OH \cdot CMe \cdot NOBz$, which forms transparent crystals melting at 98—99°. When the ethereal mother liquor from these crystals is treated with light petroleum, transparent crystals, which melt at 69—70°, are formed, but if these are kept, they gradually fall to a white powder which melts at 98°; the compound is identical with *benzoylacethydroxamic acid* prepared by the action of benzoic chloride on *acethydroxamic acid*.

The main product of the reaction is, however, neutral, and consists of a mixture of *dibenzoylacethydroxamic acid*, $NAcBz \cdot OBz$, and *dibenzoylbenzhydroxamic acid*, $NBz_2 \cdot OBz$. When the action is carried out in aqueous solution, a small amount of *benzoylethylnitrolic acid*, $NO_2 \cdot CMe \cdot N \cdot OBz$, which melts at 133°, is always produced.

When ethylic chloroformate reacts with sodium nitroethane, it appears that derivatives of *carbethoxyacethydroxamic acid*,



are formed; this crystallises in long needles, and melts at 71—72°. These compounds are accompanied by *carbethoxyethyl-nitrolic acid*, $NO_2 \cdot CMe \cdot NO \cdot COOEt$, which is the main product of the action; it can be prepared by the action of ethylic chloroformate

mate on ethylnitrolic acid, and is a yellowish oil, boiling at 143—144° (pressure = 17 mm.). The author considers that the nitroparaffins have the general formula $\text{R}\cdot\text{CH}\cdot\overset{\text{O}}{\underset{\text{O}}{\text{N}}}\cdot\text{OH}$, and criticises the views of Hantzsch and Schultze (this vol., i, 353). A. H.

Action of Nitric acid on Aliphatic Aldehydes. By GIACOMO PONZIO (*J. pr. Chem.*, 1896, [2], 53, 431—432).—From analogy with the action of nitric acid on ketones (Fileti and Ponzio, *Abstr.*, 1895, i, 499), the author expected that by substituting aldehydes for ketones, oximidoaldehydes would be formed, which would break up into keto-aldehydes and dinitrohydrocarbons; this seems to be the course of the change, although the final products are fatty acids, hydroxylamine, and dinitrohydrocarbons. Thus, *œnanthaldehyde* yielded dinitrohexane, hydroxylamine, and heptonic acid.

A. G. B.

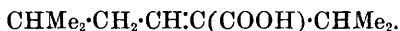
Action of Alcoholic Potash on Isovaleraldehyde. By LEOPOLD KOHN (*Monatsh.*, 1896, 17, 126—148).—The author has previously shown (this vol., i, 10) that no secondary glycol is formed by the action of alcoholic potash on valeraldehyde, the chief products being two oily substances which are best separated by fractional distillation under diminished pressure. A small quantity of isovaleric acid is formed at the same time. One of these oils, which distils at 86° (20 mm. pressure), or at 187—191° (746 mm. pressure), is a mobile liquid, and has a strong odour; it is an unsaturated aldehyde, $\text{C}_{10}\text{H}_{18}\text{O}$, but as it is very readily oxidised by atmospheric oxygen, it is almost impossible to obtain it free from the corresponding acid, $\text{C}_{10}\text{H}_{18}\text{O}_2$. This aldehyde is beyond doubt identical with the substance described by Barbier and Bouveault (*Abstr.*, 1895, i, 644), and also by Gäss. It yields an *oxime*, $\text{C}_{10}\text{H}_{18}\cdot\text{N}\cdot\text{OH}$, which is a colourless liquid boiling at 125° (20 mm. pressure), and this, when treated with acetic anhydride, yields the *nitrile*, $\text{C}_{10}\text{H}_{17}\text{N}$, a colourless, mobile oil, with a penetrating odour. The nitrile, when hydrolysed with alcoholic potash at 180°, is converted into the acid $\text{C}_{10}\text{H}_{18}\text{O}_2$.

The *phenylhydrazone*, $\text{C}_{10}\text{H}_{18}\cdot\text{N}\cdot\text{NHPh}$, crystallises in colourless plates which melt at 133°. The unsaturated nature of the aldehyde is shown by the fact that it readily unites with bromine to form a dibromide, $\text{C}_{10}\text{H}_{18}\text{Br}_2\text{O}$.

When the aldehyde is oxidised by atmospheric oxygen, by chromic acid mixture, or by potassium permanganate, it yields the acid $\text{C}_{10}\text{H}_{18}\text{O}_2$. This is a colourless, oily liquid boiling at 140° under a pressure of 19 mm., its *calcium* salt is sparingly soluble in water, its *silver* salt, $\text{C}_{10}\text{H}_{17}\text{O}_2\text{Ag}$, is soluble in hot alcohol, and its *dibromide* crystallises from benzene in brilliant, glistening prisms, which melt at 135°, and are identical with Hell and Schoop's dibromocapric acid (*Abstr.*, 1879, 715).

The unsaturated acid, $\text{C}_{10}\text{H}_{18}\text{O}_2$, when oxidised according to Fittig's method with a 2 per cent. permanganate solution, yields a dihydroxycapric acid, which must be the $\alpha\beta$ -dihydroxy acid, since it yields no

lactone; it follows, therefore, that the acid $C_{10}H_{16}O_2$ is an $\alpha\beta$ -unsaturated acid, α -isopropyl- β -isobutylacrylic acid,



This view is supported by the fact that the aldehyde $C_{10}H_{16}O$, when oxidised with potassium permanganate, yields, besides the acid previously mentioned, small quantities of isobutyric and isovaleric acids.

The second compound obtained by the action of alcoholic potash on valeraldehyde is a colourless, oily liquid with only a faint odour; it boils at 140 — 146° under a pressure of 18 mm., and has the composition $C_{10}H_{20}O_2$. It yields an oily hydrazone, but no oxime and no acetyl derivative. J. J. S.

Syntheses by means of Zinc Chloride. By IWAN L. KONDAKOFF (*J. Russ. Chem. Soc.*, 1894, **26**, 5—20; compare Abstr., 1893, i, 382; 1894, i, 113).—The reactions taking place between ethylene hydrocarbons, like trimethylethylene, isobutylene, symmetrical methylethylene, or propylene, and acid chlorides, like acetic chloride, in the presence of a small quantity of zinc chloride are characterised by great development of heat.

With trimethylethylene, two products are obtained, one a ketone, $CMe_2Cl \cdot CHMe \cdot COMe$, is a colourless liquid, boiling at 75 — 78° under 31 mm. pressure, which, with phenylhydrazine, gives a crystalline *phenylhydrazone*, showing all the reactions of the pyrazolones. The chloroketone is broken up by alkalis into hydrogen chloride and the ketone $CMe_2 \cdot CMe \cdot COMe$, a homologue of mesityl oxide, boiling at about 147° . This energetically combines with bromine forming colourless, tabular crystals, melting at 93° . The oxime boils at 106 — 110° under 31 mm. pressure. Sodium hydrogen sulphite forms a crystalline compound with the ketone. When the ketone is distilled with dilute acids, it breaks up, similarly to mesityl oxide, into acetone and methyl ethyl ketone.

Isobutylene gives only mesityl oxide, boiling at 129 — 130° .

Symmetrical methylethylene yields secondary amylic chloride, boiling at 104 — 106° ; a saturated ketone, boiling at 195 — 200° ; and an unsaturated ketone, boiling at 153 — 159° . The latter is decomposed by acids into propaldehyde and methyl ethyl ketone, and has the structure $CH_2Me \cdot CH : CMe \cdot COMe$.

Propylene gives two products, one boiling at 38° (isopropyl chloride), the other at 80° , under 20 mm. pressure; the latter unites with bromine, but does not react with silver oxide or hydroxylamine. A β -chloroketone, $CHMeCl \cdot CH_2 \cdot COMe$, is first formed, which, losing the elements of hydrogen chloride, gives the ketone $CHMe \cdot CH \cdot COMe$, isopropyl chloride being simultaneously formed. S. G. R.

Products of the Distillation of Wood. By ERNEST BARILLOT (*Compt. rend.*, 1896, **122**, 735—736).—Experiments on an industrial scale confirm the results obtained in the laboratory (this vol., i, 403), but the yield of calcium acetate does not vary in the same way as the yield of acetic acid in the laboratory experiments, a result probably

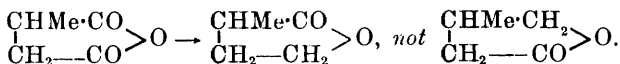
dependent on the real nature of the acids which are regarded as "acetic acid."
C. H. B.

Distillation of Acids of the Acetic Series. By E. SOREL (*Compt. rend.*, 1896, **122**, 946—948).—The author has applied to mixtures of water and each of the first four acids of the acetic series the method of fractional distillation previously applied to aqueous alcohol (Abstr., 1893, ii, 347), the composition of the vapour at each instant being calculated from the curve representing the variations in the composition of the liquid in the retort. A table is given showing the results for proportions of acid varying from 1 per cent. to 70 per cent.

In dilute solutions, the proportion of acid in the vapour is higher the higher the molecular weight of the acid, but when the concentration increases, the reverse is the case, and the proportion is lower the higher the molecular weight of the acid. As a result, mixtures of propionic or butyric acid and water of a certain composition distil unchanged, as if they were definite hydrates. Butyric acid, moreover, shows a peculiar phenomenon, and with any proportion of acid between 24 to 34 per cent. the composition of the distillate is independent of the composition of the liquid in the retort. Its behaviour is intermediate between that of miscible liquids and liquids which are partially or completely insoluble in one another.

C. H. B.

New Method of preparing Aliphatic Lactones. By FRITZ FIGHTER and A. HERBRAND (*Ber.*, 1896, **29**, 1192—1195).—Lactones may be obtained by reducing the anhydrides of appropriate dibasic acids; pyrotartaric anhydride yields α - (not β -) methylbutyrolactone.



The anhydride is dissolved in plenty of ether, the solution poured on to some lumps of 4—5 per cent. sodium amalgam in a conical flask, and a slight excess of dilute hydrochloric acid (1 : 1) run in under the ethereal solution, acid and amalgam being used in twice the theoretical amount. The yield was 10—20 per cent. of the theoretical.

In this way, succinic anhydride yields butyrolactone, and pyrotartaric anhydride yields the lactone prepared by Hjelt (Abstr., 1884, 297); this is shown to be α -methylbutyrolactone (not β), because it yields methylethylacetic acid when reduced with hydriodic acid and phosphorus. Glutaric anhydride appears to yield not a lactone, but α -hydroxyvaleric acid.

C. F. B.

Action of Ethylic Orthoformate on Ethereal Salts of Ketonic acids, on Ketones, and on Aldehydes. By LUDWIG CLAISEN (*Ber.*, 1896, **29**, 1005—1008).—Ethylic orthoformate condenses with ethylic acetoacetate under certain conditions to form *ethylic ethoxymethyleneacetoacetate*, $\text{OEt}\cdot\text{CH}\cdot\text{C}(\text{Ac})\cdot\text{COOEt}$, under others to form *ethylic ethoxycrotonate*, $\text{OEt}\cdot\text{CMe}\cdot\text{CH}\cdot\text{COOEt}$. From the latter, the *acid* can be

prepared; it readily loses carbonic anhydride, forming *isacetone ethyl ether*, $\text{OEt}\cdot\text{CMe}\cdot\text{CH}_2$, which boils at 62° . In the same way ethylic benzoylacetate, yields *ethylic β -ethoxycinnamate*,



boiling at $171\text{--}173^\circ$ under 17 mm. pressure; *β -ethoxycinnamic acid*, $\text{OEt}\cdot\text{CPh}\cdot\text{CH}\cdot\text{COOH}$, melting at 162° , with evolution of carbonic anhydride; and *ethoxystyrene*, $\text{OEt}\cdot\text{CPh}\cdot\text{CH}_2$, which boils at $209\text{--}210^\circ$, and has a sp. gr. = 0.973 at 15° . *Ethylic acetonedicarboxylate* yields *ethylic ethoxylglutaconate*, $\text{COOEt}\cdot\text{CH}\cdot\text{C}(\text{OEt})\cdot\text{CH}_2\cdot\text{COOEt}$, boiling at $146\text{--}147^\circ$ under 11 mm. pressure; the acid melts at $182\text{--}183^\circ$ with evolution of carbonic anhydride.

In reality, the first action of ethylic orthoformate on the acetoacetate is to replace the two methylene hydrogen atoms by ethoxyl groups, and by working at a low temperature a large yield of *ethylic β -diethoxybutyrate*, $\text{CMe}(\text{OEt})_2\cdot\text{CH}_2\cdot\text{COOEt}$, can be obtained. This, when distilled, splits up into alcohol and the ethoxycrotonate, and it, or rather its sodium derivative, can be formed from the ethoxycrotonate by dissolving this in alcoholic sodium ethoxide. *Sodium diethoxybutyrate* crystallises well; the free acid is unstable, and, when distilled, decomposes into carbonic anhydride and the compound $\text{CMe}_2(\text{OEt})_2$, analogous to acetal, and boiling at 114° . The last compound can be obtained more easily by the action of ethylic orthoformate on acetone. From benzophenone, however, no analogous derivative could be so prepared.

In a similar manner ethylic orthoformate acts on aldehydes, converting them into acetals, $\text{CHR}(\text{OEt})_2$. Those from benzaldehyde and from furfuraldehyde were prepared; the latter boils at $187\text{--}190^\circ$.

C. F. B.

Specific Refractive Power of Pyrotartaric acid. By ALBERT LADENBURG (*Ber.*, 1896, 29, 1254).—The following values have been obtained at 22° in aqueous solution. Per cent. of acid, 18.66 , 19.58 , 29.27 ; angle of refraction, 1.95° , 2° , and 3.112° ; sp. gr., 1.0445 , 1.045 , and 1.074 ; $[\alpha]_D = 10.01^\circ$, 9.774° , and 9.9° respectively; the mean for $[\alpha]_D = 9.89^\circ$. The concentration of the solution has very little influence on the refractive power. These values are to be substituted for those previously given (*Abstr.*, 1895, i, 449).

J. B. T.

Replacement of Carboxyl by Amidogen in Polybasic acids. By THEODOR CURTIUS and HANS CLEMM (*Ber.*, 1896, 29, 1166—1167).—The following substances have been prepared from *suberic acid*, by the reactions indicated in *Abstr.*, 1894, i, 331. The *hydrazide*,



and *azoimide*, $\text{C}_6\text{H}_{12}(\text{CO}\cdot\text{N}_3)_2$, melting respectively at $185\text{--}186^\circ$ and 25° . *Hexamethylenediethylurethane*, $\text{C}_6\text{H}_{12}(\text{NH}\cdot\text{COOEt})_2$, melting at 84° . *Hexamethylenediamine*, $\text{C}_6\text{H}_{12}(\text{NH}_2)_2$, melts at 40° and boils at $192\text{--}195^\circ$; its *hydrochloride* remains unmelted at 270° , its *dibenzoyl derivative* melts at $154\text{--}155^\circ$.

C. F. B.

Action of Light on Organic acids in presence of Uranium Salts. By HENRY FAT (*Amer. Chem. J.*, 1896, 18, 269—290).—The

equation given by Seekamp (*Annalen*, 1862, **122**, 115) as representing the action of uranyl oxalate on oxalic acid is incorrect, as it does not account for the production of formic acid or of carbon monoxide. An unpublished investigation by Harry C. Jones has shown that the acid is decomposed with production of one molecular proportion of carbonic anhydride, the nature of the precipitate subsequently formed being dependent on the relative amounts present of uranyl oxalate and free oxalic acid, but is almost always a mixture of amorphous and crystalline substances. The green crystals proved to be hydrated uranous oxalate, $U(C_2O_4)_2 + 6H_2O$, and are obtained in a pure state when a large excess of oxalic acid is present. Further, a very small quantity of uranyl oxalate suffices for the decomposition of a very large, possibly unlimited, quantity of free oxalic acid, provided the action is a continuous one. It is probable that the uranyl salt acts in some way as an oxidising agent.

In continuation of the above work, the author has carried out experiments with the following results. The brown, amorphous precipitate is also produced when a solution of uranyl oxalate is exposed to sunlight, but is not then accompanied by gaseous products; it contains 77.15–78.47 per cent. of ammonia, and cannot be a hydrated oxide, as was at first supposed, since it contains carbon. When heated alone, it evolves a small quantity of carbonic oxide, but, owing to the small percentage of carbon in the substance, its relative amount could not be ascertained. If allowed to remain in a desiccator during a few days, it changes to a yellow substance containing 8.04–8.7 per cent. of water, 74.9–75.46 per cent. of uranium, and 1.02–1.36 per cent. of carbon. As all attempts to cause the union of carbonic oxide and water in presence of ammonium salts have given negative results, it follows that the formic acid produced in the above decomposition is formed directly from the oxalic acid. The isolation of acids from the above compounds was attempted, but without success.

Solutions of potassium uranyl malonate, with or without free malonic acid, when exposed to sunlight during several days, showed no signs of decomposition. Seekamp's observation (*loc. cit.*) that succinic acid is decomposed in presence of uranium nitrate into carbonic anhydride and propionic acid was verified, but the green precipitate simultaneously formed gave, on analysis, numbers not in agreement with those required for uranous succinate. A solution of tartaric acid and uranyl nitrate gradually assumes a deep green colour when exposed to sunlight, a light green salt of uncertain character being subsequently deposited; the production of the latter is greatly promoted by heat, but in no case has gas been evolved. Acetic, propionic, and isobutyric acids, when exposed to direct sunlight in presence of uranium salts, are decomposed into the corresponding hydrocarbons and carbonic anhydride. A. L.

A peculiar class of Platinic Compounds and the Isomeric Platoso-oxalic acids. By ALFRED WERNER (*Zeit. anorg. Chem.*, 1896, **12**, 46–54).—The author has examined a series of salts of the formula $PtPyCl_3R$ and $PtPyCl_2R$ (where Py = pyridine, R = K, Li, or

Na), which are analogous to the salts $\text{Pt}(\text{CN})_4\text{Cl}_2\text{K}_2$ and $\text{Pt}_4(\text{CN})_4\text{Br}_2\text{K}_2$ examined by Hadow (this journal, 1860, **13**, 106). When chlorine is passed into a concentrated solution of the salt, PtPyCl_3K , a magma of beautiful, copper-coloured leaflets is at first obtained, and on further treatment with chlorine a precipitate of silky, bright yellow needles of the salt PtPyCl_5K is formed. When a small quantity of the salt PyPtCl_5K is added to a solution of the salt PyPtCl_3K , the above copper-coloured compound is at once formed. By the action of bromine on the salt PyPtCl_3K , analogous compounds containing bromine are obtained.

The salt $\text{NH}_3\text{PtCl}_5\text{K}$ behaves in a similar manner; when a small quantity of the salt $\text{NH}_3\text{PtCl}_5\text{K}$ is added at a certain temperature of the solution, a compound crystallising in lustrous, green leaflets is deposited, but is converted into the salt $\text{NH}_3\text{PtCl}_3\text{K}\cdot\text{H}_2\text{O}$ as the mixture cools.

When platinisodium oxide is treated with oxalic acid at temperatures below 100° , the copper-coloured salt described by Doebereiner (*Ann. Phys. Chem.*, 1832, **27**, 243), together with a small quantity of a bright yellow salt, is formed; the latter can also be obtained from the former by heating the solution with a small quantity of sodium hydroxide. The yellow salt is reconverted into the copper-coloured salt by treatment with chlorine. A salt crystallising in yellowish-red needles is obtained by boiling platinisodium oxide with oxalic acid, and when this salt is mixed with the yellow salt the copper-coloured salt is obtained. From these results, the author concludes that the copper-coloured modification of sodium platoso-oxalate is not isomeric with the yellow modifications, but that these are additive compounds of platoso-oxalates and platinoxalates. E. C. R.

Formation of Carbon Chains: III. Reaction of Ethylic Chloracetate with Ethylic Sodiomalonate and Sodacetoacetate. By CARL A. BISCHOFF (*Ber.*, 1896, **29**, 966—971).—It is known that when an attempt is made to prepare the derivative $\text{CHR}(\text{COOEt})_2$ by the action of RX [$\text{X} = \text{Cl}, \text{Br}, \text{or I}$] on ethylic sodiomalonate, $\text{CHNa}(\text{COOEt})_2$, a certain amount of the compound $\text{CR}_2(\text{COOEt})_2$ and $\text{CH}_2(\text{COOEt})_2$ is formed at the same time, if the radicle R has a "negative" character; for example, CH_2Ph or CPh_3 . This may be ascribed to a migration of the sodium atom to the compound $\text{CHR}(\text{COOEt})_2$, when this has been formed, under the attracting influence of the negative group R. If this explanation be correct, it should be possible, by the action of ethylic chloracetate, on the sodiomalonate, to get not only the normal condensation product $\text{COOEt}\cdot\text{CH}_2\cdot\text{CH}(\text{COOEt})_2$, but also some of the compound $(\text{COOEt}\cdot\text{CH}_2)_2\text{C}(\text{COOEt})_2$. This, as a matter of fact, is the case; but yet the explanation given is not sufficient, for ethylic bromopropionate yields only the normal product; stereochemical relations are obviously concerned. Ethylic sodacetoacetate behaves in much the same way as the sodiomalonate.

Methylic pentandioic-3-dimethyloate $(\text{COOMe}\cdot\text{CH}_2)_2\text{C}(\text{COOMe})_2$, which appears not to have been described before, boils at 187° .

C. F. B.

Formation of Carbon Chains: IV, V, VI. Reaction of Ethylic Sodioalkylmalonates and Sodioalkylacetoacetates with the Ethylic Salts of α -Bromo-fatty acids. By CARL A. BISCHOFF (*Ber.*, 1896, 29, 972—978, 979—982, 982—989; compare this vol., i, 84).—In order to study the comparative ease with which different radicles can be introduced into an already existing complex, the reaction which the sodium derivatives of ethylic malonate and of its methyl, ethyl, propyl, isopropyl, isobutyl, isoamyl, and allyl derivatives undergo with the α -bromo-derivatives of ethylic propionate, butyrate, isobutyrate, and isovalerate, has been examined in detail. In each case, 70 c.c. of absolute alcohol containing 4.6 grams of sodium (1 atom) in solution was mixed with the malonate (1 mol.) and the ethylic bromo-salt (1 mol.), and the mixture heated on the water bath until it became neutral to phenolphthaleïn, the eight malonic derivatives being heated separately with one of the bromo-salts in the same bath at the same time. The time that elapsed before the mixture became neutral varied greatly, but it never exceeded two hours in the case of the bromopropionate and bromobutyrate, or four in the case of the bromoisobutyrate, and was eight hours, on the average, in the case of the bromisovalerate. When the action was ended, the mixture was diluted with 50 c.c. of ether, and filtered from the salt that separated; the latter being washed with two successive quantities of 10 c.c. of ether. The combined filtrates were then heated at 100—105° until no more ether distilled over, and the residue twice distilled under atmospheric pressure, fractions being collected at intervals of 10° in the first distillation, of 5° in the final one. A curve was then constructed in which the weights of the final fractions were plotted as ordinates and the temperatures at which they boiled as abscissæ; a number of such curves is reproduced in the paper. As a rule, each curve exhibits two maxima; one near the boiling points of the two ethereal salts which were taken, the other near that of their normal condensation product. The higher the second maximum relatively to the first, the greater is the amount of condensation that has taken place. In no case was the formation of a *di*-substitution product of the malonate indicated by the curve (compare preceding abstract).

Similar experiments were made, using, instead of ethylic malonate and its above-named derivatives, ethylic acetoacetate and its corresponding derivatives.

The following conclusions are drawn from the results of the experiments. (I) All the malonic derivatives yield condensation products more readily than the corresponding acetoacetic derivatives. (II) As regards their power of condensing with malonic and acetoacetic derivatives, the ethylic bromo-salts arrange themselves in the following order of decreasing condensibility: propionic, butyric, isobutyric, isovaleric. Ethylic α -bromoisobutyrate will hardly condense with acetoacetates; it condenses in the β -position with mono-substituted malonates. (III) The malonic derivatives arrange themselves in the following order of decreasing condensibility: ethylic malonate, and then the methyl, ethyl, propyl, allyl, isoamyl, isobutyl, and isopropyl derivatives; the last hardly reacts at all. (IV) With the acetoacetic

derivatives, which react much less readily, the limit of condensibility is already reached at the ethyl derivative, which hardly yields any condensation product.

C. F. B.

Formation of Carbon Chains. VII. Conjugated Ethereal Malonates with Single Linking. By CARL A. BISCHOFF (*Ber.*, 1896, 29, 1276—1280).—Diethylic malonate and diethylic bromomalonate in presence of sodium ethoxide yield chiefly tetrethylic ethanetetracarboxylate with some tetrethylic ethylenetetracarboxylate. It is doubtful whether the hexabasic acid,



is formed even in traces; the ethylenetetracarboxylate was probably derived from a little dibromomalonate in the monobromo-compound. Under similar conditions, dimethylic malonate, methylic bromomalonate, and sodium methoxide yield dimethylic malonate, methylic ethanetetracarboxylate, and the *methylic* salt of the above hexabasic acid (*propanehexacarboxylic acid pentanedioctetramethyloic 2:3:3:4-acid*). It is separated by distillation under reduced pressure, boils at 250—255° (26 mm.), melts at 136°, is sparingly soluble, and, when hydrolysed by means of hydrochloric acid, yields tricarballic acid. These results are in complete accordance with the "dynamic" hypothesis. Methylic ethanetetracarboxylate may be readily prepared from sodium methoxide, methylic malonate, and iodine in molecular proportion; the first two are mixed, and the crystalline mass thoroughly incorporated with solid iodine, the temperature being maintained below 20°. The ethylic salt acts in a similar manner; in neither case is any hexabasic acid formed. The methylic salt, $\text{OH} \cdot \text{C}[\text{CH}(\text{COOMe})_2]_3$, obtained by Zelinsky and Porchunow (this vol., i, 135) from diethylic sodiomalonate and carbon tetrachloride, is probably identical with the above salt of the hexabasic acid.

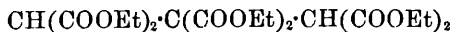
J. B. T.

Formation of Carbon Chains. VIII. Conjugated Dimethylic Malonates with Double Linking. By CARL A. BISCHOFF (*Ber.*, 1896, 29, 1280—1286).—Sodium methoxide and dimethylic bromomalonate readily react; the chief product is the propanehexacarboxylic acid, $(\text{COOR})_2\text{CH} \cdot \text{C}(\text{COOR})_2 \cdot \text{CH}(\text{COOR})_2$ (compare preceding abstract), which was identified by the production of tricarballic acid when hydrolysed, but ethylenetetracarboxylic acid, is also formed. As a portion of the crude product (b. p. 150—220°, 10 mm.) when hydrolysed gives maleic acid and, in traces, fumaric acid, tetramethylic mesoxyate (b. p. 215—220°) is apparently also formed. Probably a bromo-acid, $\text{CH}(\text{COOR})_2 \cdot \text{C}(\text{COOR})_2 \cdot \text{CBr}(\text{COOR})_2$, is first produced, the group R_3CBr being then converted into R_3CH , thus: $\text{R}_3\text{CBr} + (\text{COOMe})_2\text{CHBr} + 2\text{NaOMe} = 2\text{NaBr} + \text{R}_3\text{CH} + (\text{COOMe})_2\text{C(OMe)}_2$. Ethylenetetracarboxylic acid is formed by treating tetramethylic ethanetetracarboxylate with bromine at 190° or with iodine and sodium methoxide at low temperatures. The *methylic* salt crystallises in long, thick needles or prisms, melts at 121°, and yields maleic anhydride and fumaric acid when hydrolysed. The

hexabasic acid (*loc. cit.*) is also formed in considerable quantity. Dimethylic chloromalonate differs from the bromo-derivative in its behaviour towards sodium methoxide; the reaction proceeds more slowly, and hydrolysis occurs to a large extent. The fraction boiling at $215-220^{\circ}$ under the ordinary pressure probably contains tetramethylic mesoxalate, which is frequently produced by the decomposition of chloromalonates. The portion boiling at about 180° (20 mm.) melts at $105-120^{\circ}$, and, when hydrolysed by means of hydrochloric acid, yields fumaric acid and, in larger quantity, succinic acid, proving that the original fraction must have contained tetramethylic ethylenetetra-carboxylate and tetramethylic ethanetetra-carboxylate respectively.

J. B. T.

Formation of Carbon Chains. IX. Conjugated Diethylic Malonates with Double Linking. By CARL A. BISCHOFF (*Ber.*, 1896, 29, 1286—1293).—The author's object was to ascertain whether in the ethylic series, in addition to or instead of the normal product, $C(COOEt)_2 \cdot C(COOEt)_2$, the hexabasic compound



is also formed, or whether the production of this is dependent on the presence of the methoxy-group; also whether differences exist between ethylic bromo- and chloro-malonate similar to those between the corresponding methylic salts. The "dynamic hypothesis" indicates that whilst the bromine favours the reaction, this tendency might be neutralised by the ethylic group.

The interaction of sodium ethoxide and diethylic chloromalonate has been studied by Conrad and Guthzeit, who obtained ethylic ethylenetetra-carboxylate together with considerable quantities of oil, amounting in some cases to 60 per cent.; ethylic ethanetetra-carboxylate was isolated in small quantity from this, but no tricarballic acid could be obtained by the hydrolysis of the highest fraction. Diethylic chloromalonate therefore behaves like the methylic salt (compare preceding abstract).

Diethylic bromomalonate and sodium ethoxide yield only tetra-ethylic ethylenetetra-carboxylate; this, by the action of phenylhydrazine, gives the phenylhydrazide described by Ruhemann (*Abstr.*, 1894, i, 14), together with ethylic ethanetetra-carboxylate, which, by the further action of phenylhydrazine, gives the same phenylhydrazide. Dipotassium dihydrogen ethylenetetra-carboxylate, obtained by the hydrolysis of the tetrethylic salt when suspended in benzene and treated with dry chlorine, yields the acid; this crystallises from ether in small, colourless, quadratic plates, and from water in short, quadratic prisms containing $1\frac{1}{2} H_2O$. The tetrapotassium salt crystallises with $2H_2O$ in hexagonal plates which quietly char when heated. The zinc salt crystallises with $4\frac{1}{2} H_2O$; when dried and then exposed to air, a salt containing $1H_2O$ is formed. These normal salts are all stable when heated, but the dipotassium salt at 150° evolves carbonic anhydride and then water; the acid when heated at $163-164^{\circ}$ evolves gas; when slowly heated, fumaric acid is formed, but if quickly heated or distilled, dimethylmaleic anhydride (pyrocinchonic

acid) is produced. The fact that ethylenetetracarboxylic acid should exhibit no tendency to form an anhydride, whilst its hypothetical decomposition product, dimethylmaleic acid, yields one so readily, is of considerable interest.

J. B. T.

Decomposition of Acid Amides. By HUGO WEIDEL and E. ROITHNER (*Monatsh.*, 1896, **17**, 172—190; compare A. W. Hofmann, *Abstr.*, 1882, 822, 950, 1052; 1883, 789; 1884, 1114; Hoogewerff and van Dorp, *Abstr.*, 1886, 1194; 1889, 981; 1891, 196 and 1216).—Succinamide when treated with potash and bromine in quantities required by the equation $C_4H_6N_2O_2 + 2KOH + 4Br_2 = C_4H_5N_2O_2 + 2KBr + 2H_2O$, yields a substance isomeric with α -lactylcarbamide (Urech, *Annalen*, **165**, 99), which the author terms β -lactylcarbamide. The yield, if too much hypobromite is not used and if the temperature is kept low, amounts to 55—60 per cent. It crystallises in brilliant, glistening, prismatic needles, melts at 275° (uncorr.), and is very sparingly soluble in cold water or alcohol, but readily in hot; ether and benzene even when hot dissolve only minute quantities. In chemical properties, the substance behaves like a weak monobasic acid; the sodium and potassium derivatives are extremely deliquescent; the silver compound, $C_4H_5AgN_2O_2$, is a colourless precipitate, consisting of minute crystals, and is almost insoluble in hot water. When heated with acetic anhydride, it yields a *monacetyl* derivative, which crystallises in colourless, glistening, monoclinic needles, melts at 180° (uncorr.), and is readily soluble in warm alcohol or ethylic acetate.

If β -lactylcarbamide is heated with concentrated hydrochloric acid in sealed tubes at 160°, it is decomposed into β -amidopropionic acid, carbonic anhydride, and ammonia; when treated with alcohol, β -amidopropionic acid hydrochloride is converted into *ethylic* β -amidopropionate hydrochloride, which is readily soluble in alcohol and water, but insoluble in ether; it melts at 69—71° (uncorr.), and the yield is almost theoretical. Concentrated aqueous soda decomposes β -lactylcarbamide in a similar manner. The author has succeeded in synthesising β -lactylcarbamide by heating equivalent quantities of carbamide and β -amidopropionic acid, first at 180°, and then at 210—220°. The amide of pyrotartaric acid, prepared by Henry's method (*Abstr.*, 1886, 886), melts at 225°, and not at 175° (Henry), and when treated with potassium hypobromite, yields β -methyl- β -lactylcarbamide, $CHMe < \begin{smallmatrix} NH \cdot CO \\ CH_2 \cdot CO \end{smallmatrix} > NH$; this is a colourless syrup, and also yields a syrupy *acetyl* derivative. When heated with concentrated hydrochloric acid at 160°, it is decomposed into β -amidobutyric acid, carbonic anhydride, and ammonia.

β -Amidobutyric acid crystallises in colourless needles, melts at 184° (uncorr.), is insoluble in absolute alcohol and in ether, and yields a well-defined *platinochloride*, $(C_4H_7NO_2)_2 \cdot H_2PtCl_6$. When treated with nitrous acid, it is converted into a syrupy hydroxybutyric acid, and this, if acted on with phosphorus pentachloride and then with alcohol, yields Balbiano's ethylic β -chlorobutyrate.

Malonamide is completely destroyed when treated with potassium

hypobromite, but when malonamide (1 mol.) is treated first with bromine (1 mol.), and then, after some time, with dilute potash (1/5 normal), until neutral, and when the crystalline compound thus obtained is warmed with potash, hydantoic acid is formed; the yield is, however, very poor. J. J. S.

Action of Carbamide and Thiocarbanilide on Acid Anhydrides. By FREDERICK L. DUNLAP (*Amer. Chem. J.*, 1896, **18**, 332—341).—Phthalimide is the sole product of the interaction of phthalic anhydride and carbamide at 150° (compare Piutti, *Abstr.*, 1882, 1297) and is thus readily obtained in a pure condition. *Dichloromaleïnuric acid*, $\text{COOH}\cdot\text{CCl}\cdot\text{CCl}\cdot\text{CO}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2$, is produced when a mixture of dichloromaleïc anhydride and carbamide in molecular proportions is heated at 90—95° for 20 minutes; it crystallises from alcohol in transparent prisms with truncated ends, and melts and decomposes at 158°. It is very sparingly soluble in all ordinary solvents with the exception of hot water. The product of its decomposition at 158° is dichloromaleimide, which is also formed directly when the mixture of dichloromaleïc anhydride and carbamide is heated at 110—115° for 15 minutes. Carbamide and dichloromaleïc anhydride, when heated together at 100—105°, yield *dibromomaleïnuric acid*, $\text{COOH}\cdot\text{CBr}\cdot\text{CBr}\cdot\text{CO}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2$; this is insoluble in light petroleum, benzene, carbon bisulphide, and water, but dissolves in alcohol, chloroform, and ether, and is readily soluble in acetone; it separates from alcohol in tufts of prisms with doubly truncated terminations; it melts and decomposes at 191°, yielding dibromomaleimide, which may be conveniently obtained by heating a mixture of dibromomaleïc anhydride and carbamide at 135°. Succinimide is readily obtained by distilling a mixture of succinic anhydride and carbamide; the intermediate product, succinuric acid, melts at 211—211.5°, and not at 203—205° as stated by Pike (this Journal, 1874, **27**, 49).

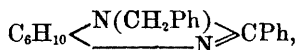
Thiocarbanilide and phthalic anhydride interact at 125—130°, the products being phthalanilic acid, and phenylthiocarbimide; diphenylthiophthaluric acid, probably the intermediate substance, could not be isolated. At 170—175° the products are phthalanil, thiocarbonic anhydride, and aniline. Phthalanilic acid is insoluble in benzene, chloroform, light petroleum, and ether, very sparingly soluble in acetone, but is slightly soluble in boiling water; Laurent and Gehrhardt gave its melting point as 192°, Zincke and Cooksey (*Abstr.*, 1890, 784) as 158°, and J. F. Thorpe (*Abstr.*, 1893, i, 466) as 191—193°. The authors now find that the substance, prepared by several methods, always melts at 169—169.5°, simultaneously evolving gases and forming phthalanil, which melts at 204°.

Thiocarbanilide and succinic anhydride at 130—150° give thiocarbonic anhydride, succinanil and aniline, together with a substance sparingly soluble in hot alcohol and melting at 226°; a small quantity of phenylthiocarbimide is formed at 130—135°. A. L.

Condensation of Aldehydes with Ethylic Acetonedicarboxylate. By PAVEL I. PETRENKO-KRITSCHENKO and S. STANIS-

CHEWSKY (*Ber.*, 1896, **29**, 994—996).—*Ethyllic dimethyltetrahydropyronedicarboxylate*, $\text{CO} < \begin{smallmatrix} \text{CH}(\text{COOEt}) \cdot \text{CHMe} \\ \text{CH}(\text{COOEt}) \cdot \text{CHMe} \end{smallmatrix} > \text{O}$, is formed when gaseous hydrogen chloride is led into a mixture of ethylic acetonedicarboxylate (1 mol.) and acetaldehyde (2 mols.). It melts at 102° , and boils at $195\text{--}200^\circ$ under 68 mm. pressure; it gives a red coloration with alcoholic ferric chloride; it is not acted on by boiling acetic chloride or phosphorus trichloride, but the pentachloride reacts with it at 100° . The corresponding *diphenyl* compound was prepared in a similar manner, using benzaldehyde; it melts at 115° , and reacts like the dimethyl compound; a bye-product, melting at 148° , was also obtained. C. F. B.

Orthohexamethylenediamine. By ALFRED EINHORN and BENJAMIN S. BULL (*Ber.*, 1896, **29**, 964—965).—Ethylic hexahydroanthranilate (*Abstr.*, 1894, i, 591) yields the *amide* when treated with alcoholic ammonia. This melts at $153\cdot5^\circ$, and, when its hydrobromide is oxidised with hypobromite, loses 2 atoms of hydrogen, yielding the compound $\text{C}_7\text{H}_{12}\text{N}_2\text{O}$; this melts at $230\text{--}232^\circ$, reduces Fehling's solution, and yields a nitroso-derivative. Its constitution is as yet undetermined; it is stable towards alkalis, but treatment with hydrochloric acid readily converts it into *orthohexamethylenediamine*, $\begin{smallmatrix} \text{CH}_2\text{CH}_2\text{CH}\cdot\text{NH}_2 \\ | \\ \text{CH}_2\text{CH}_2\text{CH}\cdot\text{NH}_2 \end{smallmatrix}$, of which the *dihydrochloride* was prepared, and also the condensation product with benzaldehyde, namely, hexahydro-orthophenylenebenzylamidine,



melting at $132\cdot5^\circ$.

C. F. B.

Sandmeyer's Reaction. By JOHANN WALTER (*J. pr. Chem.*, 1896, [2], **53**, 427—430).—Votoček has stated (*Chem. Zeit. Rep.*, 1896, **20**, 70), that the quantity of cuprous chloride may be reduced to 1/21 and 1/28 mol. per mol. of amine without appreciably influencing the yield of chlorobenzene and metachloronitrobenzene respectively in the well-known reaction. The author holds the view that the mechanism of the change consists in the reduction of diazobenzene chloride to phenylhydrazine by the cuprous chloride which thus becomes cupric chloride; the phenylhydrazine is then oxidised in the presence of hydrochloric acid to chlorobenzene by the cupric chloride; the cuprous chloride would thus be again formed to take its part in the cycle of changes once more. It was found that phenylhydrazine in presence of hydrochloric acid is oxidised to chlorobenzene by both cupric chloride and ferric chloride; and although it was found impossible to detect phenylhydrazine as an intermediate product in the Sandmeyer reaction, this may be because it is oxidised as soon as formed. In the fact that a copper salt is not essential to the production of iodobenzene by this method, the author sees a confirmation of his view, since hydriodic acid is itself a reducing agent.

A. G. B.

Isomerism in the Benzene Series. By WILLIAM OECHSNER DE CONINCK (*Compt. rend.*, 1896, **122**, 736—737).—The author has previously shown (*Abstr.*, 1894, i, 289, 333, 464) that isomerides in the benzene series arrange themselves in pairs with respect to solubilities and some of their chemical properties. This holds good also in the case of melting and boiling points:—

Dichlorobenzenes, boiling points, *ortho* 179°, *meta* 172°, *para* 173°.

Chloronitrobenzenes, boiling points, *ortho* 243°, *para* 242°, *meta* 233°.

Chlorotoluenes, boiling points, *ortho* 156—157°, *meta* 156—157°, *para* 160—161°.

Bromonitrobenzenes, melting points, *ortho* 42°, *meta* 56°, *para* 126—127°.

Diphenols, melting points, *ortho* 104°, *meta* 110°, *para* 169°.

Hydroxybenzoic acids, melting points, *ortho* 155·5°, *meta* 200°, *para* 210°.

C. H. B.

Stability of Halogen Derivatives of Benzene. By C. LORING JACKSON and SIDNEY CALVERT (*Amer. Chem. J.*, 1896, **18**, 298—312).—1 : 3 : 5 : 2-Tribromiodobenzene, contrary to the statements of Silberstein (*Abstr.*, 1883, 660), is less volatile than 1 : 3 : 5-tribromobenzene; it is most conveniently prepared by acting with hydriodic acid on the corresponding tribromodiazobenzene sulphate. When dissolved in benzene and heated with an alcoholic solution of sodium ethoxide during one hour, it is decomposed with production of 1 : 3 : 5-tribromobenzene together with a brownish-yellow powder, which melts above 300°, and is not completely soluble in any of the usual media. Hot sodium methoxide or cold sodium ethoxide effect only a partial decomposition of the substance, whilst sodium phenoxide, aqueous soda, sodium carbonate, moist zinc oxide, aniline, or ethylic sodiomalonate are without action; alcoholic soda, however, gives a large quantity of tribromobenzene. That the elimination of the iodine is due to the influence of the bromine atoms is shown by the stability of iodobenzene towards boiling alcoholic sodium ethoxide.

Iodine is liberated when cold fuming nitric acid is caused to act on 1 : 3 : 5 : 2-tribromiodobenzene, and the latter is converted into 1 : 3 : 5 : 2 : 4-tribromodinitrobenzene, $C_6HBr_3(NO_2)_2$, melting at 191°.

1 : 2 : 3 : 5-Tetrabromobenzene and 1 : 3 : 5 : 2-tribromochlorobenzene are slowly attacked by boiling sodium ethoxide, 1 : 3 : 5-tribromobenzene being produced as before, but in much smaller quantity, 1 : 2 : 4 : 5-tetrabromobenzene, under similar conditions, suffers partial conversion into 1 : 2 : 4-tribromobenzene.

The authors have convinced themselves of the correctness of Blau's observation (*Abstr.*, 1887, 242) that symmetrical tribromobenzene is converted into dibromophenylic ethylic ether by sodium ethoxide, and find that this agent attacks tetrabromodinitrobenzene [$(NO_2)_2 = 2 : 4$] giving the tribromonitroresorcinol diethyl ether first obtained, together with what was in all probability trinitrophenyl glucinol triethyl ether, by acting on tribromotrinitrobenzene with sodium ethoxide (*Abstr.*, 1891, 1024).

From the above data, the authors conclude that, whilst in respect to the loosening effect on substituting atoms or groups situated in

the benzene nucleus, nitro-groups are more powerful than halogen atoms, yet the effect produced by a halogen, in the ortho- or para-position with regard to the group in question, is not inconsiderable. A satisfactory explanation of the curious decomposition of symmetrical tribromotrinitrobenzene is made possible on this supposition.

A. L.

Cis- and Trans-Modifications of Benzene Hexabromide. By WILLIAM R. ORNDORF and V. A. HOWELLS (*Amer. Chem. J.*, 1896, **18**, 312—319).—Benzene hexabromide, as obtained by Meunier's method (*Abstr.*, 1885, 1126), consists of the pure α -modification, but when prepared according to the directions of Matthews (*Trans.*, 1893, **61**, 110) this is accompanied by β -benzene hexabromide; in the latter case, the substances may be separated by means of chloroform in which the β -compound is practically insoluble.

α -Benzene hexabromide forms monoclinic crystals, $a : b : c = 0.9938 : 1 : 0.5268$; $\beta = 69^\circ 22'$ (compare Des Cloizeaux, *Ann. Chim. Phys.*, [6], **10**, 269).

β -Benzene hexabromide crystallises in the cubic system, and shows octahedral and rhombic dodecahedral forms. It is more sparingly soluble in chloroform, benzene, toluene, and metaxylene than the corresponding α -compound, and is nearly insoluble in alcohol and ether. When heated with alcoholic potash, it affords, quantitatively, unsymmetrical tribromobenzene. It melts and decomposes at 253° .

α -Benzene hexabromide is in all probability the *trans*-compound; it presents in its properties a complete analogy with the *trans*-hexachloride. The β -hexabromide is doubtless the *cis*-modification, although it differs in crystalline symmetry from the corresponding hexachloride.

A. L.

Preparation of Paraethyltoluene. Two Isomeric Barium Salts of Paraethyltoluenesulphonic acid. Two Methylparaethylphenols. By PIERRE H. BAYRAC (*Bull. Soc. Chim.*, 1895, [3], **13**, 889—894).—The author describes the method of preparation of paraethyltoluene from parabromotoluene and ethylic iodide by Fittig's reaction. By heating the paraethyltoluene with $2\frac{1}{2}$ times its weight of concentrated sulphuric acid on the water bath for four hours, and saturating with barium carbonate, two barium salts are obtained; one, the β -salt, crystallises with $3\text{H}_2\text{O}$ in needles, and is very soluble in water; the other, the α -salt, crystallises with $2\text{H}_2\text{O}$ in prisms, and is less soluble in water. He considers them to be derivatives of the two sulphonic acids [$\text{Me} : \text{Et} : \text{SO}_3\text{H} = 1 : 4 : 2$ and $1 : 4 : 3$]

By converting these barium salts into the corresponding potassium derivatives, and fusing with potash, the corresponding phenols are obtained. The α -phenol boils at 225.5 — 226.5° (corr.), has sp. gr. = 0.99665 at 21° , and is a caustic liquid, only slightly soluble in water. The β -phenol boils at 219.8 — 220.8° (corr.).

J. F. T.

Cryoscopic Experiments with Salts of Phenols. By HEINRICH GOLDSCHMIDT and OTTO GIRARD (*Ber.*, 1896, **29**, 1224—1242).—When the weak monobasic phenols, such as ordinary phenol, metacresol, thymol, and α - and β -naphthol are added to dilute caustic soda

solution, they lower the freezing point of the latter. The extent of this lowering is such as would correspond with the complete electrolytic dissociation of the salts formed, and in some cases even exceeds this. Since, however, it is unlikely that the salts of these phenols should either be completely dissociated or hydrolysed to the extent required to account for these results, the phenomenon remains at present without explanation. More strongly acid phenols, such as orthonitrophenol, quinone-oxime, β -naphthaquinone-oxime, and hydroxyazobenzene, on the other hand, do not lower the freezing point of dilute caustic soda, but raise it, since the salts formed are dissociated to a less extent than caustic soda. The more strongly acid dibasic phenols, such as resorcinol, quinol, and dioximidoresorcinol also raise the freezing point of dilute caustic soda, but to a greater extent than might be calculated from the general equation $2\text{Na} + 2\text{OH} + \text{XHH} = 2\text{Na} + \text{X} + 2\text{H}_2\text{O}$, according to which the introduction of a single molecule of the dibasic phenol causes the disappearance of two hydroxyl ions. Catechol is much less acid than its isomerides, and chiefly forms the monosodium salt, its disodium salt being hydrolysed to a very large extent. The sodium salt of dioximidoresorcinol is dissociated to a much smaller extent than those of the dihydroxy-phenols.

In the case of hydroxy-oximes, such as oximidoresorcinol, the oxime hydroxyl is the first to react. Oximidobenzeneazoresorcinol acts as a well-marked dibasic phenol, whilst the isomeric benzene-azoximidoresorcinol behaves as a monobasic phenol. A. H.

Iodine Derivatives of Anisoil. Migration of an Iodine Atom. By FRÉDÉRIC REVERDIN (*Ber.*, 1896, 29, 997—1005).—2-Iodanisoi was prepared by the diazo-reaction from orthanisidine; it is a heavy oil, boiling at $239\text{--}240^\circ$ under 730 mm. pressure. When it is nitrated at 0° with a mixture of fuming nitric and acetic acids, it yields 2:4-iodonitranisoi, $[\text{OMe} : \text{I} : \text{NO}_2 = 1 : 2 : 4]$, which melts at $95\text{--}96^\circ$; a red bye-product melting at $63\text{--}64^\circ$ is also formed. This nitro-compound, when reduced with stannous chloride, yields 2:4-iodanisidine, which melts at $74\text{--}75^\circ$; the *platinochloride* melts at 207° , the *thiocarbamide* at $194\text{--}195^\circ$, and the *acetyl derivative* at $152\text{--}153^\circ$; it yields paranisidine when reduced with sodium amalgam in alcoholic solution, and can be converted by the diazo-reaction into 2:4-diiodanisoi, which melts at $68\text{--}69^\circ$.

4-Iodanisoi, prepared by the diazo-reaction from paranisidine, melts at $51\text{--}52^\circ$, and boils at 237° under 726 mm. pressure. When nitrated it yields, in addition to a yellow substance (4:2-iodonitroanisoi?) melting at 73° , and a substance melting at 87° , 2:4-iodonitroanisoi, in all respects identical with the substance obtained from 2-iodanisoi. The identity was further proved by crystallographic examination of the picrates of the two iodanisidines obtained by reducing the two samples; the two picrates were found to be identical, and to crystallise in the rhombic system ($a : b : c = 1.7800 : 1 : 0.5265$). A migration of the iodine atom from the 4 to the 2 position must thus have taken place during the nitration.

These iodo-compounds have no very marked physiological action.

The ortho- moniodo-compounds are more powerful antiseptics and local irritants than are those with the iodine in the para position. A second iodine atom weakens the effect.

C. F. B.

Action of Sodium on Phenyl γ -Bromopropyl Ether.

By BASIL M. SOLONINA (*J. Russ. Chem. Soc.*, 1894, **26**, 1—5).—Phenyl γ -bromopropyl ether, $\text{CH}_2\text{Br}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OPh}$, was obtained by the action of an excess of trimethylene bromide on sodium phenoxide, the ether being distilled under a pressure of 200 mm., when it boiled at $211\text{--}212^\circ$; 35 per cent. of the theoretical quantity was obtained. The sp. gr. of the ether = 1.365 at $16^\circ/16^\circ$. It was added to metallic sodium under a layer of absolute ether, taking care to keep the mixture cool; after some days, the solution was filtered from the sodium bromide and sodium phenoxide, treated with water, the ether distilled off, and the residue recrystallised from 95 per cent. alcohol. The substance obtained in this way melts at 83° ; the long, needle-shaped crystals are very soluble in ether, benzene, and chloroform, fairly so in hot 95 per cent. alcohol, but only sparingly in cold alcohol. The analysis gave numbers corresponding with the formula $\text{C}_6\text{H}_{12}(\text{C}_6\text{H}_5\text{O})_2$, which is that of the diphenyl ether of hexamethyleneglycol. This was confirmed by a molecular weight determination by Raoult's method. The corresponding iodide and bromide, $\text{C}_6\text{H}_{12}\text{I}_2$ and $\text{C}_6\text{H}_{12}\text{Br}_2$, were obtained from it by the action of hydriodic and hydrobromic acids.

S. G. R.

Two Modifications of Mononitroso-orceinol [Oximido-orceinol]. By FR. HENRICH (*Ber.*, 1896, **29**, ii, 989—993).—Krämer (Abstr., 1884, 1340) and Nietzki and Mackler (Abstr., 1890, 763) have prepared two modifications of monoximido-orceinol,



without noticing the fact. Their method of preparation was adopted, except that the potassium, instead of the sodium, derivative was prepared. If a hot aqueous solution (1 : 10) of this substance is treated with boiling, dilute sulphuric acid (1 : 3), and the mixture allowed to cool, dark red crystals are formed. If an aqueous solution (1 : 12) is cooled with ice and treated with dilute sulphuric acid, an orange-red, flocculent precipitate is momentarily formed, but this changes at once into a yellow powder. The red substance carbonises at $110\text{--}112^\circ$ when impure, but when pure it is transformed at $100\text{--}110^\circ$ into the yellow variety, and then turns brown at $157\text{--}162^\circ$, finally melting, or occasionally exploding. The red substance is monoclinic and strongly dichroic, whereas the yellow variety is not dichroic and is optically uniaxial—probably tetragonal. The yellow (α) variety is the stable one, and is formed from the red variety (β), when a current of hot air is passed over the latter; it is possible, however, to effect a partial transformation of the yellow into the red variety, by boiling down a solution in some solvent that boils under 100° , such as acetone. It is difficult to say what is the nature of the isomerism of the two

substances, for they yield identical derivatives; namely, when reduced, a base with the hydrochloride $C_7H_7O_2 \cdot NH_2 \cdot HCl + 2H_2O$; when nitrated, a dinitro-orsinol melting at $164-165^\circ$; and with acetic anhydride, an *acetyl derivative*, $C_7H_6AcNO_2 + 2H_2O$, which softens at 115° , and melts at $119-120^\circ$.
C. F. B.

Safrole and Isosafrole. By CHARLES MOUREU (*Compt. rend.*, 1896, **122**, 792—795).—Methylenecatechol [orthomethylenedioxybenzene], $C_6H_4 \cdot \begin{smallmatrix} O \\ \diagup \diagdown \end{smallmatrix} CH_2$, obtained by the action of methylene iodide on disodium catechol, is an oily, colourless liquid which has an aromatic odour, and boils at $172-173^\circ$; sp. gr. = 1.202 at 0° . When treated with allylic iodide and zinc powder, it would doubtless yield safrole.

If isosafrole really has the constitution usually attributed to it, it ought to be formed by the action of heat on methylenebromocaffeic acid (Lorenz, *Abstr.*, 1881, 48). The latter is prepared by the interaction of piperonal, propionic anhydride, and dry sodium propionate, and crystallises from alcohol in small needles, which melt at $198-199^\circ$. The silver salt crystallises from boiling water in slender, white needles. When carefully heated, the methylenebromocaffeic acid begins to decompose at 270° , and yields isosafrole amongst other products. Much larger quantities are, however, formed by the decomposition of part of the methylenecaffeic acid during its preparation by the reaction indicated. The isosafrole thus obtained is identical with the natural product. These results establish the constitution usually attributed to safrole and isosafrole; the former is allylmethylenecatechol, and the latter propenylmethylenecatechol.

C. H. B.

Isosafrole Nitrosite. By ANGELO ANGELI and ENRICO RIMINI (*Gazzetta*, 1896, **26**, i, 7—12).—The isosafrole nitrosite first prepared by Angeli (*Abstr.*, 1892, 447), readily loses water, yielding a dioxide peroxide (*Abstr.*, 1892, 1198), and, on heating with water, alcohol, or, better, piperidine, it also loses water yielding a *compound*, $C_{10}H_9NO_4$, which is precipitated on passing carbonic anhydride through the piperidine solution; it is a yellow, crystalline substance melting at 98° . The aqueous mother liquors obtained during its recrystallisation subsequently deposit a white substance melting at 134° ; this is an additive *compound* with piperidine, having the composition $C_{10}H_9NO_4 \cdot C_6H_{11}N$.

On heating isosafrole nitrosite with primary bases such as aniline, resinous products are obtained, but on dissolving it in alcoholic benzylamine solution, heat is developed, and a white crystalline *product*, which melts at 76° , may be precipitated from the solution by adding water; it yields benzylamine hydrochloride and piperonal on treatment with dilute hydrochloric acid, and consequently has the constitution $CH_2O_2 \cdot C_6H_3 \cdot CH \cdot N \cdot CH_2Ph$.

Similarly, on boiling isosafrole nitrosite with alcoholic hydroxylamine hydrochloride and soda, piperonaloxime, melting at $110-112^\circ$, is obtained.

The compound of the composition $C_{10}H_9NO_4$, described above would, on the basis of the above results, seem to be piperonyl- β -nitropropylene $CH_2O_2 \cdot C_6H_5 \cdot CH \cdot CMe \cdot NO_2$, and its hydrolysis by alkalis should occur in accordance with the equation
 $CH_2O_2 \cdot C_6H_5 \cdot CH \cdot CMe \cdot NO_2 + H_2O = CH_2O_2 \cdot C_6H_5 \cdot COH + CH_2Me \cdot NO_2$;
 the authors were, however, unable to detect nitroethane amongst the products of hydrolysis.
 W. J. P.

Action of Acid Chlorides on the Silver Salts of the Anilides.

By HENRY L. WHEELER and B. B. BOLTWOOD (*Amer. Chem. J.*, 1896, **18**, 381—389).—*Benzoformanilide*, $CHO \cdot NPhBz$, is prepared by adding benzoic chloride (1 mol.) to dry silver formanilide (1 mol.) suspended in benzene; it crystallises in colourless needles, melts at 112° , and dissolves readily in benzene and chloroform, less so in ether and alcohol, and with difficulty in water; treatment with sodium hydroxide removes the formyl group, yielding benzanilide.

2 : 4-*Dichloroformanilide* was prepared by chlorinating acetanilide according to the method of Beilstein and Kurbatow (*Annalen*, **196**, 215), and replacing the acetyl group by the formyl group in the usual manner. It crystallises in colourless needles, and melts at 153° . The silver compound, $C_6H_3Cl_2 \cdot NAg \cdot CHO$, is described; by treating this with benzoic chloride, *benzoformo-2 : 4-dichloranilide* is obtained; it crystallises in prisms, melts at 77° , and dissolves readily in benzene and hot alcohol, but only sparingly in water.

Benzo-2 : 4-dichloranilide, formed by boiling formobenzo-2 : 4-dichloranilide with hydrochloric acid, melts at 117° , and dissolves sparingly in hot water, but freely in hot alcohol and ether.

Benzoforthotoluidide, prepared like benzoformanilide, crystallises in thick rectangular plates, melts at 92° , and dissolves freely in benzene and warm alcohol, but with difficulty in water; treatment with sodium hydroxide converts it into benzorthotoluidide.

Silver formanilide and ethylic chlorocarbonate react to form, among other products, ethylisoformanilide (Comstock and Clapp, *Abstr.*, 1892, 707) which, when mixed with 2 : 4-dichloraniline, yields *phenyl-2 : 4-dichlorophenylformamidine*, $NPh \cdot CH \cdot NH \cdot C_6H_3Cl_2$; this crystallises in aggregates of colourless plates, and melts at 159° . *Ethylic orthotolylformimido-ether*, $C_6H_4Me \cdot N \cdot CH \cdot OEt$, is an aromatic oil, boiling at 101° under a pressure of 12 mm.
 A. G. B.

Nitration of Dimethylparatoluidine. By PIETER VAN ROMBURGH (*Ber.*, 1896, **29**, 1015—1016).—Pinnow's contention (this vol., i, 161) that the author's method does not give a homogeneous product is incorrect. In the first place, the author did not dissolve his dimethylparatoluidine in acetic acid, and in the second, even if this is done, a homogeneous product can be obtained quite easily.

The dinitrotolylmethylnitramine formed is converted by boiling with a little phenol into dinitromethyltoluidine. This, when heated with sodium nitrite in nitric acid solution, yields dinitrotolylmethyl-nitrosamine; and this exchanges its nitroso-group for a nitro-group when boiled with fuming nitric acid, and for hydrogen when boiled with phenol.
 C. F. B.

Action of Propylic, Butylic, and Amylic Sodiocyanacetates on Diazobenzene Chloride. By G. FAYREL (*Compt. rend.*, 1896, 122, 844—846).—The direct action of propylic, butylic, and amylic sodiocyanacetates on diazobenzene chloride yields the corresponding benzeneazocyanacetates, $\text{Ph}\cdot\text{N}_2\cdot\text{CH}(\text{CN})\cdot\text{COOR}$. These are obtained in the α -modification by crystallisation from light petroleum, and in the β -modification by treating the former in different ways.

Propylic Benzeneazocyanacetate.—The α -modification forms slender, pale yellow needles, melts at 78 — 80° , and is converted into the β -modification by melting, and crystallising from hot, light petroleum. The latter forms elongated yellow prisms, and melts at 102 — 103° . When crystallised from strong solutions or from cold benzene, the crystals are rhomboïdal or hexagonal plates with the same melting point.

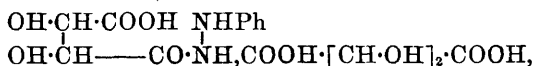
Butylic Benzeneazocyanacetate.—The α -modification forms very light, silky, pale yellow needles, which melt at 118 — 120° . When dissolved in sodium hydroxide, and precipitated by carbonic anhydride, it is converted into the β -modification, which crystallises from benzene in pale yellow prisms melting at 98 — 101° .

Amylic Benzeneazocyanacetate.—The α -modification crystallises from light petroleum in very pale, yellow needles, which melt at 77 — 78° , but if boiled for some time, the solution, on cooling, deposits the β -modification in yellow prisms, which melt at 57 — 59° .

It will be seen that the propyl-, butyl-, and amyl-sodiocyanacetates behave in the same way as their lower homologues, and it is noteworthy that the melting point of the product (except in the case of the butylic derivatives) decreases from methyl to amyl in the case of both the α - and β -modifications. C. H. B.

Phenylhydrazine Tartrate and its Derivatives. By HENRI E. CAUSSE (*Compt. rend.*, 1896, 122, 940—942).—Phenylhydrazine hydrogen tartrate is obtained in colourless, prismatic needles by adding 100 grams of phenylhydrazine to a solution of 100 grams of tartaric acid in 500 c.c. of strong alcohol, and then adding to the liquid its own volume of ether at 65° . The product is purified by crystallisation from boiling alcohol; it melts and decomposes at 118 — 119° , and is somewhat feebly lævogyrate. The hydrogen tartrate most probably has the constitution $\text{H}\cdot\text{C}_4\text{H}_6\text{O}_6\cdot\text{NPh}\cdot\text{NH}\cdot\text{C}_4\text{H}_6\text{O}_6\cdot\text{H}$; it behaves as a dibasic acid towards bases, and forms an amido-derivative and a hydrochloride. The potassium salt forms small, white crystals only slightly soluble in cold water, and insoluble in alcohol and ether, the aqueous solution being lævogyrate; the barium salt forms white, microscopic crystals, and its aqueous solution is lævogyrate; the antimonyl (SbO) salt forms small, silky crystals, soluble in water, but less soluble in alcohol, both solutions being lævogyrate.

The amido-derivative,



is obtained by heating the salt at 100° . It forms small crystals, which melt at 225° , and are only slightly soluble in water and alcohol,

but the solutions are more strongly lævogryrate than those of the hydrogen tartrate.

The hydrochloride is obtained by the direct action of hydrochloric acid, and forms small crystals, the solutions of which are lævogryrate. A benzoic and an aldehydic derivative have also been prepared.

C. H. B.

Behaviour of Opianic acid and its Ethereal Salts with Reagents for Aldehydes. By RUDOLF WEGSCHEIDER (*Monatsh.*, 1896, 17, 111—120; compare Abstr., 1895, i, 420, and Liebermann, this vol., i, 232).—With a solution of magenta decolorised with sulphurous acid, the acid itself gave little or no red coloration, the true methylic salt a red colour, and the ψ -methylic salt no colour.

With diazobenzeneparasulphonic acid, potash solution and 4 per cent. sodium amalgam, all three give a violet-red coloration, that with the acid is the strongest, the true methylic salt comes next, and the ψ -salt is weakest.

By treating opianic acid with pyruvic acid and β -naphthylamine, Liebermann's β -naphthylamide of opianic acid is formed; this melts at 207—207.5° (Liebermann gives 213°), and is almost insoluble in ether and hot water. Doebner's α -methyl- β -naphthocinchonic acid (Abstr., 1894, i, 261, 532) is formed at the same time; it melts at 290° (Doebner gives 310°).

Both the acid and ψ -methylic salt give meconine when reduced with acetic acid and zinc dust; the acid and both salts, with hydroxylamine, yield opianoximic acid anhydride (compare Liebermann, Abstr., 1887, 258). The action of phenylhydrazine on the three compounds is also given (compare Liebermann, Abstr., 1886, 550).

J. J. S.

Two Orthophthalic acids. By W. T. H. HOWE (*Amer. Chem. J.*, 1896, 18, 390—401).—The variation in the melting point of phthalic acid as determined by different observers is due to the existence of two isomeric forms of the acid, distinguished in this paper as α -phthalic acid, which melts at 203°, and β -phthalic acid, which melts at 184°. Commercial phthalic acid is generally a mixture of the two, and when its aqueous solution is boiled for three to four hours, the α -acid crystallises out on cooling. Graebe's observation that the acid melts at 183—184°, if kept at this temperature for some time, is due to the formation of anhydride. The β -acid may be prepared in a pure condition by dissolving phthalic anhydride in cold dilute sodium hydroxide, cooling to 0°, slowly precipitating by hydrochloric acid, and drying the precipitate over sulphuric acid. Phthalic anhydride appears, therefore, to be derived from the β -acid. The α -acid yields the β -form when boiled with a 30 per cent. solution of sodium or potassium hydroxide for four or five hours, and then precipitating and drying as just described; the conversion is also partially effected by strong acids. The β -acid is very sensitive to warm water, easily becoming partially converted into the α -acid, but for complete conversion three or four hours' boiling is essential. Light has no effect on the β -acid. Melting points lower than that of the β -acid, observed by some investigators, are ascribed to the contamination of their specimens by acid salts.

The molecular refraction of the acids is virtually identical, but the electrical conductivity of the α -acid is lower than that of the β -acid. 100 parts of absolute alcohol at 20° dissolve 11.74 parts, and at 23° 14.08 parts of the α -acid, whilst the same quantity of solvent dissolves 14.12 parts of the β -acid at 20°, and 16.18 parts at 23°.

The following table shows the differences between some salts of the two acids.

Salt.	α -acid.	β -acid.
Aniline.....	Plates, m. p. 160°	Plates, m. p. 147—148°
α -Naphthylamine.	Prisms, m. p. 163°	Needles, m. p. 155°
Quinoline.....	Plates, m. p. 98°	Needles, m. p. 92°
Brucine.....	Prisms, m. p. 228°	Needles, m. p. 212—313°

Warm alcohol or an excess of the base quickly changes the salts of the β -acid into those of the α -acid.

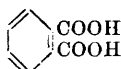
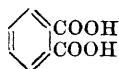
By reduction with sodium amalgam, the β -acid yields a dihydro-acid which differs in the following respects from the $\Delta_{3.5}$ acid obtained by Baeyer, from the α -acid.

	$\Delta_{3.5}$ acid.	New dihydro-acid.
Melting point	210°	195°
" " of anhydride	101—103°	126
With cold solution of } AgNO ₃	No reaction.	Reduces.
With sodium amalgam in } the cold.....	No reaction.	{ Reduces to tetra- hydro-acids.
With cupric acetate.....	{ Precipitation of cuprous oxide on addition of acetic acid.	{ Precipitation of cuprous oxide without addition of acetic acid.

Of the two tetrahydro-acids prepared by reducing the new dihydro-acid, one is the Δ^1 -tetrahydrophthalic acid (m. p. 120°), prepared by Baeyer, the other is a new acid, and melts at 206°.

Several metallic salts of α - and β -orthophthalic acids have been prepared; in many cases they differ in form and in their content of water of crystallisation. The α -salt is more stable than the β -salt, and the latter is converted into the former by boiling with water.

The author is of opinion that these acids are cases of the single and double bond isomerism required by Kekulé's benzene formula, and heretofore regarded as a stumbling-block to the acceptance thereof. The acids would be represented by the formulæ

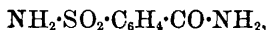


A. G. B.

Transformations of Parasulphaminebenzoic acid when heated. By IRA REMSEN and ARTHUR M. MUCKENFUSS (*Amer. Chem. J.*, 1896, 18, 349—365).—When parasulphaminebenzoic acid is heated for three hours at 285°, the mass becomes coloured, and is freely

soluble in water and alcohol, but not in benzene, ether, and light petroleum. The aqueous solution contains ammonium hydrogen parasulphobenzoate almost exclusively; in view of this fact, and that there is no loss of weight when the acid is heated, the authors believe that the ammonium salt is formed by the hydrolysis of benzaminesulphonic acid, $\text{NH}_2 \cdot \text{CO} \cdot \text{C}_6\text{H}_4 \cdot \text{SO}_3\text{H}$, which may be supposed to constitute the immediate product of the action of heat on parasulphaminebenzoic acid, $\text{COOH} \cdot \text{C}_6\text{H}_4 \cdot \text{SO}_2 \cdot \text{NH}_2$, having been formed by a migration of the nitrogen atom analogous to that which occurs in the conversion of ammonium cyanate into urea or that of benzil-dioxime into oxanilide (compare this vol., i, 372).

When heated at $220-235^\circ$ for eight hours, and then treated with water, parasulphaminebenzoic acid yields an insoluble compound which may be purified by dissolution in dilute caustic soda, treatment in the cold with animal charcoal, and acidification with hydrochloric acid, which causes the separation of characteristic crystals of the new compound. This substance is infusible, and, since its analysis gives figures which agree with the formula



and its properties indicate that it is an amide, it is referred to as the infusible diamide. It does not dissolve in any of the usual solvents; strong sulphuric acid dissolves it readily, and when the solution is diluted the infusible diamide is precipitated in small plates, even though the solution has been heated to 200° . It is unchanged by heating with phosphorus pentachloride at 200° for several hours; concentrated hydrochloric acid at 200° converts it into ammonium hydrogen parasulphobenzoate and ammonium chloride, a small quantity of an insoluble compound being formed at the same time. The infusible diamide loses the whole of its nitrogen as ammonia when treated with caustic soda, even at low temperatures.

To compare the properties of this supposed diamide with that of the diamide of parasulphobenzoic acid, the latter was prepared in the usual manner; it dissolves readily in boiling water and in alcohol; it melts sharply at 230° . The action of hydrochloric acid on this diamide is similar to that of the acid on the infusible diamide; sodium hydroxide expels half the nitrogen from the fusible diamide, producing parasulphaminebenzoic acid.

The aqueous solution of the product obtained by heating parasulphaminebenzoic acid at $220-235^\circ$, filtered from the insoluble diamide, contains ammonium hydrogen parasulphobenzoate, parasulphobenzoic acid, and a compound intermediate in solubility between these two, and called *isoparasulphaminebenzoic acid*. The barium salt of this acid crystallises in sparingly soluble needles, with $3\text{H}_2\text{O}$, remarkable for the manner in which they fill the mother liquor. The free acid is very soluble in water; it gives up its nitrogen with difficulty when heated with potassium hydroxide solution, a fact at variance with the supposition that the acid may be benzaminesulphonic acid, since this would contain a CONH_2 group which is known to easily lose nitrogen as ammonia. Isoparasulphaminebenzoic acid is less easily attacked by hydrochloric acid than is parasulphamine-

benzoic acid, but yields the same products; attempts to prepare the amide were not successful.

This investigation is being continued.

A. G. B.

New Synthesis of Phenanthridine Bases. By AMÉ PICTET and A. HUBERT (*Ber.*, 1896, **29**, 1182—1189).—When orthamidodiphenyl (Abstr., 1894, i, 529) is treated with the anhydride of a fatty acid or with benzoic chloride, a derivative, $C_6H_5 \cdot C_6H_4 \cdot NH \cdot CRO$, is formed, and this, when heated with 3—4 times its weight of zinc chloride at 250—300°, yields a phenanthridine, $C_6H_4 < \begin{smallmatrix} C_6H_4 \\ CR \end{smallmatrix} > N$.

These phenanthridines were purified by precipitation as mercurichlorides; the phenyl compound, however, by crystallising the hydrochloride. They are colourless, and form colourless salts with colourless acids; the aqueous solutions of salts with mineral acids, except those of the phenyl derivative, exhibit a faint blue fluorescence. Phenanthridine itself (Abstr., 1890, 390) and its methyl, ethyl, and phenyl derivatives were prepared by this method. In the following list of new compounds described, the numbers indicate melting points (often points of decomposition, also, in the case of salts), except where the contrary is stated.

Formamidodiphenyl, 75°. *Acetamidodiphenyl*, 117°; boils at 335° (uncorr.). *Propionamidodiphenyl*, 65°; boils about 350°. *Benzamidodiphenyl*, 85—86°. *Methylphenanthridine*, 85°; boils above 360°: *hydrochloride*, 285°; *platinochloride* (with 2H₂O), flesh-coloured, 272°; *aurochloride*, yellow, 163—164°; *mercurichloride*, 247°; *picrate*, yellow, 233°; *methiodide*, 246—247°. *Ethylphenanthridine*, 54—55°: *hydrochloride*, 205°; *platinochloride*, with 2H₂O, yellow, 241—242°; *aurochloride*, yellow, 149°; *mercurichloride*, 214°; *picrate*, yellow, 210°. *Phenylphenanthridine*, 109°; boils above 400°: *hydrochloride* (with H₂O) melts at 95—96°, then solidifies, and melts again at 220°; *nitrate*, 205°; *platinochloride*, with 2H₂O, yellow; *mercurichloride*, yellow (?), 220°; *picrate*, yellow, 242°.

Ethylic chloroformate acts on orthamidodiphenyl, forming *diphenylurethane*, $C_6H_5 \cdot C_6H_4 \cdot NH \cdot COOEt$. This melts at 186°, and yields phenanthridone, $C_6H_4 < \begin{smallmatrix} C_6H_4 \\ CO \end{smallmatrix} > NH$ (Abstr., 1893, 658), when heated with zinc chloride.

C. F. B.

Condensation Products of Hydroxydiphenylethylamine. By HENRIK G. SÖDERBAUM (*Ber.*, 1896, **29**, 1210—1216; compare Abstr., 1895, i, 596).—Carbonyl chloride reacts with diphenylhydroxyethylamine in toluene solution to form 4 : 5-*diphenyl-2-ketodihydro-1 : 3-azoxole*, $\begin{smallmatrix} CHPh \cdot NH \\ | \\ CHPh - O \end{smallmatrix} > CO$, which crystallises in slender, matted needles melting at 189—189·5°. It is insoluble in dilute acids and alkalis. *Hydroxydiphenylethylurethane*, $OH \cdot CHPh \cdot CHPh \cdot NH \cdot COOEt$, is formed by the action of ethylic chloroformate on the same base. It crystallises in colourless needles melting at 148—148·5°, and is converted at 275° into the foregoing compound, with elimination of ethylic alcohol. Carbon bisulphide converts the diphenyl base into 4 : 5-*di-*

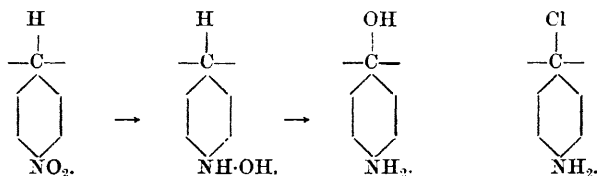
phenyl-2-thiodihydro-1 : 3-azoxole, $\begin{matrix} \text{CHPh}\cdot\text{N} \\ \text{CHPh}\cdot\text{O} \end{matrix} \gg \text{C}\cdot\text{SH}$, which crystallises in stellate groups of tablets, and melts at 185° . This compound has distinct acid properties, and dissolves in cold, dilute aqueous soda. It is readily attacked by oxidising agents. *Hydroxydiphenylethylamine formate* crystallises in white, nacreous plates, which melt and decompose at 182° . *Formylhydroxydiphenylethylamine*, $\text{C}_{14}\text{H}_{14}\text{NO}\cdot\text{CHO}$, is obtained by heating the foregoing substance, and crystallises in needles which melt at $182\text{--}183^\circ$. The *di-formyl* derivative is prepared by the continued action of formic acid on the base, and forms vitreous needles which melt at 208° . *Acetylhydroxydiphenylethylamine* melts at $196\text{--}197^\circ$; the *diacetyl* derivative crystallises in short, four-sided prisms, and melts at $212\text{--}213^\circ$. The isomeric *diacetyl* derivative, which is stated by Goldschmidt and Polonowska to melt at 159° (Abstr., 1887, 492), does not appear to exist. *Acetylisohydroxydiphenylethylamine* melts at $152\text{--}153^\circ$. *Benzoylhydroxydiphenylethylamine* forms slender, matted needles, and melts at $236\text{--}237^\circ$; the *dibenzoyl* derivative melts at 254° . This compound is accompanied by about 26 per cent. of *dibenzoylisohydroxydiphenylethylamine*, which melts at $186\text{--}187^\circ$. Since the original base was free from iso-compound, it appears that partial molecular change must occur under the influence of the benzoic chloride which is used for the preparation.

A. H.

Reduction of Nitrotetramethyldiamidotriphenylmethane.

By MAURICE PRUD'HOMME (*Bull. Soc. Chim.*, 1895, [3], **13**, 913—915).—When nitrotetramethyldiamidotriphenylmethane is reduced by means of zinc dust and hydrochloric acid, the curious fact is noticed that, if the acid is in excess, a violet colouring matter, capable of dyeing cotton mordanted with tannin, silk, or wool, is directly produced, without any subsequent oxidation.

This the author explains in the following way. The nitro-group is first reduced to $\text{NH}\cdot\text{OH}$, and the action of hydrochloric acid on this group tends to make the hydroxyl migrate to the para-position in the benzene nucleus. This position is, however, already occupied, it therefore takes the place of the hydrogen in the methyl group, which can be regarded as opposite to the group $\text{NH}\cdot\text{OH}$.



The further action of hydrochloric acid converts this into the coloured salt.

In support of this theory, the author has succeeded in isolating the phenylhydroxylamine, which, on treatment with hydrochloric acid, yields the violet colouring matter.

J. F. T.

Sulphonated Colouring Matters of the Triphenylmethane Series. "Patent Blue." By MAURICE PRUD'HOMME (*Bull. Soc. Chim.*, 1895, [3], 13, 905—913).—From the following considerations the

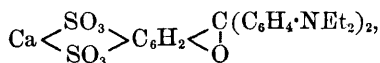
author inclines to the formula $\text{Ca} \langle \text{SO}_3 \rangle \text{C}_6\text{H}_2(\text{OH}) \cdot \text{C}(\text{C}_6\text{H}_4 \cdot \text{NEt}_2)_2 \cdot \text{OH}$.

for the dye "Patent blue." (1) The dye does not precipitate barium chloride, and therefore does not contain the acid radicle directly combined to the methane carbon atom, as in the case of the sulphates of rosaniline and similar bases. (2) In the hydrolysis with sodium hydroxide, no sodium sulphate is produced. (3) It decomposes ammonium salts in the cold, and therefore contains hydroxyl directly combined with the methane carbon atom.

The alkaline solution, after being decolorised by sodium hydroxide and exactly neutralised in the cold, becomes re-coloured slowly on standing in the cold, but quickly on warming. The re-coloration is, therefore, not due to etherification but to simple hydrolysis.

"Patent blue" is only decolorised by a concentrated solution of sodium hydroxide after standing some days. After prolonged boiling, decomposition ensues, diethylamine vapour being evolved, and a sulphonated aurine produced; this substance is characterised by having the hydroxyl groups in the *meta*- instead of the *para*-positions. It is closely analogous to ordinary aurine, dyeing silk a pale yellow.

The solution of "Patent blue" decolorised by sodium hydroxide in the cold, shows the following properties. (1) Diluted with water and warmed on the water bath with zinc dust for from 5 to 10 hours, it regenerates the leuco-derivative of the blue. (2) On being made acid with excess of acetic acid and treated with lead peroxide, it yields tetrethylbenzidine. From these data, coupled with the fact that the original colouring matter is regenerated from the decolorised solution on standing, and therefore by hydrolysis, the author considers the formula of the decolorised compound to be



that is to say, the action of the sodium hydroxide has effected a condensation with elimination of water.

An analogy is also drawn between "Patent blue" and "Helvetia green," the difference between them being merely that the former contains an additional hydroxyl in the *meta*-position. The base of "Helvetia green" shows the same reactions as the "Patent blue." It is decolorised by sodium hydroxide, slowly in the cold, rapidly on warming. On standing the colour reappears. With lead peroxide in a solution of acetic acid, tetrethylbenzidine is produced.

The corresponding formula for this decolorised compound would therefore be $\text{O} \text{C}(\text{C}_6\text{H}_4 \cdot \text{NEt}_2)_2$.

J. F. T.

Triphenylethanone and Triphenylethanolone. By MAURICE DELACRE (*Bull. Soc. Chim.*, 1895, [3], 13, 857—862).—The author has for some years held the view that benzopinacolone has the symme-

trical formula $O < \begin{smallmatrix} \text{CPh}_2 \\ | \\ \text{CPh}_2 \end{smallmatrix}$, and not the ketonic formula CPh_3COPh , usually applied to it. He has therefore attempted to prepare the latter compound, but without success. By the action of benzene on trichloroacetic chloride in the presence of aluminium chloride, only *triphenylethanone* (diphenylacetophenone), CHPh_2COPh , is produced. This substance, already prepared by Saint-Pierre, crystallises from acetic acid in white needles, melting at 135° , and distilling at $270\text{--}280^\circ$ (40 mm.). It combines with hydroxylamine only under certain conditions, and does not appear to yield a hydrazone. It has a negative hydrogen atom, readily replaceable by metals of the alkali group; the resulting compound does not, however, combine with bromobenzene with the formation of the tetraphenyl derivative sought for. The *bromo-derivative*, $\text{CPh}_2\text{BrCOPh}$, is prepared by adding the calculated quantity of bromine to a solution of the triphenylethanone in carbon bisulphide. It crystallises from light petroleum in slender, transparent needles, melting at 97° . Attempts to substitute a phenyl group for the bromine atom by Friedel and Craft's reaction were unsuccessful, the compound being simply reduced.

Triphenylethanolone, $\text{OH}\cdot\text{CPh}_2\text{COPh}$ (diphenylhydroxyacetophenone), is produced by acting directly on triphenylethanone with bromine, and separating the product with water. It forms silky tufts melting at 84° . The *acetate* forms fine, vitreous crystals, melting at $145\text{--}146^\circ$. J. F. T.

Isomeric Acetylaurins. By JOSEF HERZIG (*Monatsh.*, 1896, 17, 191—198; compare Herzig and von Smoluchowski, *Abstr.*, 1894, i, 336).—From the alcoholic mother liquor obtained in the preparation of acetylaurin (*loc. cit.*), the author has isolated a substance which melts at $146\text{--}149^\circ$, and is isomeric with acetylaurin. Both acetyl derivatives when hydrolysed yield aurin, and this, when again acetylated, gives a mixture of the two acetyl derivatives. The isomeride of low melting point is readily converted into that of higher melting point by dissolving it in acetic acid, and allowing the solution to remain for some time. The author thinks this isomerism is similar to the isomerism observed by Baeyer among the hydrophthalic acids.

J. J. S.

Peridinitronaphthalene. By CH. GASSMANN (*Ber.*, 1896, 29, 1243—1246).—The author describes several methods of nitrating naphthalene with the object of obtaining the best yield of 1 : 1'-dinitronaphthalene. The largest amount, 67.9 of the theoretical yield, is obtained by bringing 128 grams of naphthalene in the cold into a mixture of 260 grams of nitric acid of 61.7 per cent. with 300 grams of 92 per cent. sulphuric acid and 200 grams of fuming sulphuric acid containing 60 per cent. of anhydride. After shaking well, the whole is heated for 12 hours on the water bath. The 1 : 1'-compound is then extracted from the mass by acetone, and recrystallised.

A. H.

Derivatives of the Naphthylamines. By CARL BOETTINGER (*Arch. Pharm.*, 1896, 234, 170—185; 185—194; compare *Abstr.*, 1895, i, 106).—*Mono-β-naphthylamine succinate* is the only product

formed when β -naphthylamine and succinic acid are dissolved in alcohol. It crystallises in slightly brownish needles, melts at 132—133°, and is partially decomposed by boiling with water.

Succino- β -naphthalide, $C_2H_4(CO \cdot NH \cdot C_{10}H_7)_2$, which is obtained by heating the base with succinic acid, crystallises in very small needles, is only sparingly soluble in boiling alcohol, and melts at 264°. Acetic anhydride does not yield an acetyl derivative, but converts it into *succino- β -naphthil*, $C_2H_4 \langle \begin{smallmatrix} CO \\ CO \end{smallmatrix} \rangle N \cdot C_{10}H_7$, which forms prismatic crystals, melts at 176°, but solidifies again at a few degrees above this temperature, and then melts again at 183—184°.

Pyruvic- β -naphthil is formed along with a little dinaphthylamine when pyruvic acid is heated with β -naphthylamine; it crystallises in rosettes of small prisms, and melts at 158—159°.

Glycollic- α -naphthalide is converted by benzoic chloride into a *benzoyl* derivative, which crystallises in broad needles melting at 191—191.5°. *Glycollic- β -naphthalide* crystallises in large, colourless prisms, and melts at 138—139°. The *benzoyl* derivative forms needles, which melt at 163°. An acetyl derivative could not be obtained.

Normal β -naphthylamine tartrate crystallises in large, white plates, with a silvery lustre, and melts at 170—171°.

Tartaric- β -naphthalide is a white powder, which is almost insoluble in alcohol, and melts at 264—265°. Acetic anhydride converts it into *acetyltartaric- β -naphthalide*, which melts at 229—230°, and *diacetyltartaric- β -naphthalide*, which crystallises in compact, hard prisms, and melts at 226°.

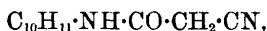
When molecular proportions of citric acid and β -naphthylamine are mixed in alcoholic solution, *mono- β -naphthylamine citrate* crystallises out in silky needles, melting at 92°. When 2 mols. of the base are mixed with one of the acid, on the other hand, an *isomeric salt*, which melts at 138°, but resembles the first in appearance, is formed. When 3 mols. of the base are employed, an *additive compound* of the mononaphthylamine salt, with 4 mols. of base, is formed. This crystallises in white chalk-like masses, melts at 114°, and readily loses β -naphthylamine at a higher temperature. When citric acid is heated with β -naphthylamine, the *anhydride* of *citric-di- β -naphthalide* is produced along with the *β -naphthylamine salt* of *citric-dinaphthalide*. The former of these is obtained in small, hard crystals, melting at 235—236°. When boiled with acetic anhydride for some time, it is converted into a yellowish, crystalline powder, which melts at 192°, and gives an intense yellowish-red coloration with alcoholic soda. The β -naphthylamine salt of citric dinaphthalide is a greyish-yellow powder, melting at 150—151°.

When *succino- β -naphthil* is boiled with alcoholic soda, it yields the sodium salt of *β -naphthalidosuccinic acid*. The free acid crystallises in long, lustrous needles or broad plates, and melts at 181—182°. The *calcium salt* forms slender needles, whilst the *barium salt* crystallises in compact needles. *β -Naphthalidopyruvic acid* crystallises in needles, and melts at 158—159°. The *calcium* and *barium* salts are both crystalline, as are also the corresponding salts of α -naphthalidopyruvic acid.

α -Naphthalidopyruvic acid is converted by oxidation with potassium permanganate into its components, which then undergo partial oxidation, free pyruvic acid being also found among the products. α -Dinaphthalidocitric acid undergoes an analogous change when treated in the same way.

β -Naphthylamine dichloracetate crystallises in large, colourless plates, melting at 153° . When it is heated with naphthylamine, hydrogen chloride is eliminated, and a yellow, crystalline substance is formed, which has not been obtained pure. When β -naphthylamine is heated with salicylic acid or gallic acid, it is converted into dinaphthylamine. The same change occurs when the base is heated with glyceric acid, but the dinaphthylamine is accompanied by *glyceric β -naphthalide*, which crystallises in plates, and melts at 161 – 162° . The *benzoyl* derivative melts at 130 – 131° . A. H.

Action of Ethylic Cyanoacetate on alc-Tetrahydro- β -naphthylamine. By A. BENEDICENTI (*Chem. Centr.*, 1895, ii, 973; from *Ann. Chim. Farm.*, 22, 433–440).—These two compounds react together in the cold, *cyanoacetotetrahydro- β -naphthylamide*,



being formed; it crystallises in long, colourless needles, melts at 175 – 176° , and, when oxidised with potassium permanganate, yields *tetrahydro- β -naphthylloxamic acid*, $\text{C}_{10}\text{H}_{11}\text{NH}\cdot\text{CO}\cdot\text{COOH}$, which crystallises from water in small crystals, and melts at 163 – 164° .

If the amine is first treated with acetone and then with ethylic cyanoacetate, it yields 1- β -tetrahydronaphthyl-3-cyanotrimethylpiperidone, $\text{C}_{10}\text{H}_{11}\cdot\text{N} < \begin{smallmatrix} \text{CO}\cdot\text{C}(\text{CN}) \\ \text{CMe}_2\cdot\text{CH}_2 \end{smallmatrix} > \text{CMe}$, which crystallises in long needles, melts at 210 – 211° , and, on oxidation, yields two crystalline compounds, which are being further investigated. In its physiological action, it resembles tetrahydronaphthylamine and not cyanotrimethylpiperidone. J. J. S.

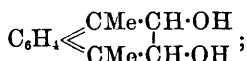
Dimethylnaphthol obtained from the Santonous acids. By STANISLAO CANNIZZARO and AMERICO ANDREOCCHI (*Gazzetta*, 1896, 26, i, 13–35).—The dimethylnaphthol obtained by the decomposition of the santonous acids (Abstr., 1895, i, 424) has the constitution $[\text{Me}_2 : \text{OH} = 1 : 4 : 2]$, and boils at 315 – 316° in a current of carbonic anhydride under ordinary pressure. The acetodimethylnaphthylamide derived from it melts at 219 – 220° , and the dimethylnaphthylamide at 75° ; the *hydrochloride* of the latter crystallises in colourless needles, and the *platinochloride* in yellow prisms; the *sulphate* was also prepared. The *formyl* derivative of the amine, obtained by heating it with formic acid, crystallises in needles, melting at 175° ; the amine is quantitatively reduced to the original dimethylnaphthol by aqueous nitrous acid, and, on oxidation with alkaline permanganate, yields azodimethylnaphthalene and phthalic acid; the latter acid is also obtained by oxidising the dimethylnaphthol.

1 : 4-Dimethylnaphthalene is prepared by the action of sodium

nitrite and stannous chloride on an alcoholic solution of the corresponding dimethylnaphthylamine saturated with hydrogen chloride; it is a colourless liquid heavier than water, and boils at 262·5—263° under 742 mm. pressure. It has the normal vapour density by V. Meyer's method, and yields a *picrate*, $C_{12}H_{13}C_6H_3N_3O_7$, which crystallises in long, yellow needles, melting at 139—141°.

The oxydimethylnaphthol previously described (*loc. cit.*), crystallises in beautiful, anorthic prisms, melting at 104—105°, and may be distilled without decomposition; $a : b : c = 0·8797 : 1 : 0·7877$; $\alpha = 90^\circ 18'$; $\beta = 98^\circ 22'$; $\gamma = 54^\circ 31'$. It is not optically active in solution, and has the normal molecular weight in freezing benzene; on heating with red phosphorus and hydriodic acid, or on warming with stannous chloride and tin in alcoholic solution, it yields the original dimethylnaphthol. It consequently has the constitution

$C_6H_4 \ll \begin{array}{c} CMe \cdot CO \\ | \\ CMe \cdot CH \cdot OH \end{array}$, and, on reduction, probably gives as intermediate product a dihydroxy-compound of the formula



this, however, could not be isolated.

The *phenylhydrazone*, $C_6H_4 \ll \begin{array}{c} CMe \cdot C \cdot N \cdot NPh \\ | \\ CMe \cdot CH \cdot OH \end{array}$, of oxydimethylnaphthol is readily obtained, and crystallises in long, red needles, melting at 83—84°. The *oxime*, $C_6H_4 \ll \begin{array}{c} CMe \cdot C \cdot N \cdot OH \\ | \\ CMe \cdot CH \cdot OH \end{array}$, crystallises in small prisms, melting and decomposing at 175° when rapidly heated; it yields a white, crystalline *acetyl* derivative, $C_{14}H_{15}NO_3$, which melts at 116—117°, and has the normal molecular weight in freezing acetic acid.

2 : 1 : 4-Nitrosodimethylnaphthalene is prepared by heating an acetic acid solution of the oxime; it crystallises in long, green needles, melting at 99—100°, is very soluble in organic solvents, and gives the normal molecular weight by the cryoscopic method in benzene solution. It is converted into the 1 : 4 : 2-dimethylnaphthylamine by reduction with zinc dust and acetic acid, and into 2 : 1 : 4-azodimethylnaphthalene by heating with 1 : 4 : 2-dimethylnaphthylamine in alcoholic solution.

Bisnitrosodimethylnaphthalene, $C_{24}H_{22}N_2O_2$, is obtained by the action of alcoholic potash on nitrosodimethylnaphthalene; it crystallises in transparent, yellow needles, melting at 174—175°, and is shown to have the molecular composition given above by boiling point determinations in benzene solution. It is accompanied by a small proportion of a *substance* crystallising in yellow laminæ, melting at 205°, and yields an *acetyl* derivative, $C_{24}H_{21}N_2O_2Ac$, in white crystals, melting at 182°. Bisnitrosodimethylnaphthalene is converted into a *substance* of the composition $C_{24}H_{20}N_2O$ by heating with alcoholic potash; it crystallises in white prisms, melting at 180° with preliminary alteration.

W. J. P.

A new Hydrocarbon, $C_{14}H_{12}$. By P. SCHICKLER (*J. pr. Chem.*, 1896, [2], 53, 369—374).—This hydrocarbon is prepared by dropping benzylic ethylic ether into a flask provided with a reflux apparatus, and containing a mixture of benzene with phosphoric anhydride; the mixture is at first kept hot on the water bath, but is cooled when the reaction begins to be violent. Ethylene is evolved, and the liquid assumes a blue fluorescence. After distilling off the benzene and fractionating the residue, a clear, colourless, aromatic liquid is obtained, which can be crystallised by cooling. The new hydrocarbon, $C_{14}H_{12}$, forms thick, hard prisms, the odour of which recalls that of benzylic ethylic ether. It melts at $27-28^{\circ}$, boils at $253-254^{\circ}$, and dissolves in all the usual solvents; solutions of the pure hydrocarbon show no fluorescence. In the absence of benzene, benzylic ethylic ether and phosphoric anhydride react to form a resinous mass of crystalline structure. When other solvents are substituted for benzene, the yield of the hydrocarbon is very poor. Benzylic ether and benzylic alcohol also yield the hydrocarbon when substituted for benzylic ethylic ether in the foregoing prescription.

By nitration, the hydrocarbon yields three nitro-compounds, two of which are crystalline, and appear to be dinitro-compounds, melting at 181° and 108° respectively, whilst the third melts at 75° , but could not be obtained in crystals. Strong sulphuric acid sulphonates and dissolves the hydrocarbon. Beyond these two reactions, the author did not succeed in obtaining any specific compounds from the hydrocarbon, the nature of which, therefore, is not yet elucidated.

A. G. B.

Extraction of Terpenic Alcohols from Essential Oils. By ALBIN HALLER (*Compt. rend.*, 1896, 122, 865—869).—In order to extract the terpenic alcohols which exist in essential oils either in the free state or in the form of ethereal salts, advantage may be taken of the ease with which they combine with the anhydrides of certain dibasic acids, and the tendency of the ethereal salts to decompose. Two methods of treatment are available, but in either case the ethereal salts must first be decomposed by means of alcoholic potash, and the product dried over anhydrous sodium sulphate.

In the first method, the essential oil is heated with the calculated quantity of succinic or phthalic anhydride, either alone or in presence of a hydrocarbon, so that an ethereal hydrogen salt is formed. The product is extracted with a concentrated solution of sodium carbonate, and the alkaline liquid, previously exhausted with ether, is heated on a water bath with excess of sodium hydroxide until no more oil is liberated. Another plan is to acidify the alkaline liquid and separate the ethereal hydrogen salt. In either case, the product is treated with alcoholic potash, and the oil that separates is dried and purified by fractionation.

The second method is applicable to alcohols that would be dehydrated by the acid anhydrides. The dried oil is dissolved in ether or benzene, mixed with a quantity of sodium corresponding with the quantity of alcohol present, and, after removal of any unattacked metal, a quantity of succinic or phthalic anhydride, corresponding

with the sodium dissolved, is added. When the action is complete the product is treated with water, and the undissolved oil is washed with a dilute solution of an alkali; the aqueous solutions are washed with ether, and treated as in the first method. Before applying the second method, any aldehydes must be removed, or they will be reduced by the action of the sodium.

Experiments with several varieties of oil of geranium, oil of peppermint, and oil of spike show that the methods give a good yield of the alcohols present.

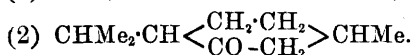
C. H. B.

Homolinalol and the Constitution of Licareol and Licarhodol. By PHILIPPE BARBIER and LOUIS BOUVEAULT (*Compt. rend.*, 1896, **122**, 842—844).—Methylheptenone, when treated with zinc and allylic iodide, yields a tertiary alcohol, as Tiemann and Schmidt have stated. The best yield is obtained if the mixture is allowed to heat spontaneously up to 40—50°. The *methylhexenylallylcarbinol* (*dimethyl-2 : 6-octadiene-2 : 7-ol-6*) produced is a colourless liquid, which boils at 99—101° under a pressure of 100 mm.; its acetate boils at 110—111° under the same pressure, and yields the original alcohol when hydrolysed.

The authors have repeated the reaction with a number of ketones analogous to methylheptenone, and in all cases have obtained stable tertiary alcohols, which react with acetic anhydride above 150° only, but yield normal acetates from which the original alcohol can be regenerated. In no case is there a conversion into an isomeride analogous to the conversion of licareol into licarhodol. From these results, it would seem that the constitution previously ascribed to licareol is not correct, and having regard to the close connection between licareol and licarhodol on the one hand, and geranaldehyde and methylheptenone on the other, the authors provisionally adopt the constitution $\text{CMe}_2\cdot\text{CH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CHMe}\cdot\text{C}(\text{OH})\cdot\text{CH}_2$ for licareol, and $\text{CMe}_2\cdot\text{CH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CHMe}\cdot\text{CH}\cdot\text{CH}\cdot\text{OH}$ for licarhodol (see Abstr., 1895, i, 77).

C. H. B.

Rhodinaldehyde and its Conversion into Menthone. By PHILIPPE BARBIER and LOUIS BOUVEAULT (*Compt. rend.*, 1896, **122**, 737—739).—When rhodinol (Abstr., 1895, i, 78) is oxidised with chromic mixture, the product is a mixture of rhodinaldehyde (this vol., i, 446) and menthone. The *semicarbazone* of the former is soluble in ether, melts at 115°, and is not affected by hydrochloric acid, whilst that of the latter is insoluble in ether, and is decomposed by hydrochloric acid. The spontaneous oxidation of oil of pelargonium yields a similar mixture of rhodinaldehyde and menthone, and not a mixture of two ketones as stated in a former paper (Abstr., 1895, i, 4). The same mixture is obtained by the spontaneous oxidation of rhodinol, and the menthone results from an isomeric change in the rhodinaldehyde. If the oxime of a mixture of rhodinaldehyde and menthone is treated with acetic anhydride, it is completely converted into the oxime of menthone. It follows that rhodinaldehyde has the constitution (1) and menthone the constitution (2):



C. H. B.

Citronellaldehyde and its Isomerism with Rhodinaldehyde.

By PHILIPPE BARBIER and LOUIS BOUVEAULT (*Compt. rend.*, 1896, **122**, 795—796).—Citronellaldehyde (Abstr., 1893, i, 685), obtained from "essence of citronelle, balm-mint of the Indies," forms a *semicarbazone*, which crystallises in micaceous lamellæ, melting at 82°. Citronellic acid is obtained from the nitrile, which is itself prepared from the oxime, and it yields a *paratoluidide* which crystallises from boiling alcohol of 80° in long, slender needles, melting at 95°; whereas the paratoluidide of rhodinic acid melts at 80.5°. Energetic oxidation of citronellaldehyde yields acetone and β -methyladipic acid as well as citronellic acid, and it is, therefore, isomeric with rhodinol, and has the constitution $\text{CMe}_2\cdot\text{CH}\cdot\text{CH}_2\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CHO}$.

C. H. B.

Essential Oil of Valerian (*Valeriana officinalis*). By LOUIS OLIVIÉRO (*Bull. Soc. Chim.*, 1895, [3], **13**, 917—926).—On hydrolysing essential oil of valerian with alcoholic potash, washing the product with water, and after having extracted the wash water with ether, evaporating to a small bulk, acidifying, and distilling, acetic acid, formic acid, and traces of butyric acid are found in the distillate; they probably exist in the essence as bornylic salts.

The ethereal extract yields a *lævorotatory*, dihydric *alcohol*, $\text{C}_{10}\text{H}_{20}\text{O}_2$, melting at about 132°, $[\alpha]_D = -96^\circ$.

The insoluble portion from the hydrolysis, on fractionation, yields a large quantity of borneol. From the fraction 160—165° a hydrocarbon, $\text{C}_{10}\text{H}_{16}$, was isolated; it boils at the same temperature as a sesquiterpene, and is *lævorotatory* $[\alpha]_D = -9^\circ 20'$. J. F. T.

Structure and Stereochemistry in the Camphor Group. By OSSIAN ASCHAN (*Chem. Centr.*, 1895, ii, 967—972; from *Acta Soc. Sci. fennice*, **21**, 1—227; compare Abstr., 1894, i, 538 and 615; 1895, i, 154, 188, and 242).—In the first part of the paper, the author discusses the various formulæ, 25 in number, which have been suggested for camphor. From recent researches it follows that (1) camphor is

a ketone, $\text{C}_8\text{H}_{14} < \begin{smallmatrix} \text{CH}_2 \\ \text{CO} \end{smallmatrix}$, but can in special cases react in its tautomeric form $\text{C}_8\text{H}_{14} < \begin{smallmatrix} \text{CH} \\ \text{C}\cdot\text{OH} \end{smallmatrix}$. (2) Camphoric acid is a dicarboxylic acid, $\text{C}_8\text{H}_{14}(\text{COOH})_2$.

(3) Camphor and camphoric acid are saturated polymethylene compounds. (4) Camphor and camphoric acid con-

(1) C
tain the grouping (2) $\text{C}\cdot\overset{\text{C}}{\overset{|}{\text{C}}}\cdot\text{C}$, in which the carbon atoms 1, 2, and 3
(3) $\text{C}\cdot\overset{\text{C}}{\overset{|}{\text{C}}}\cdot\text{C}$
are partially or completely saturated with hydrogen.

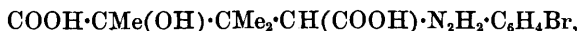
From a study of the number of the stereoisomeric camphoric acids (see Abstr., 1894, i, 538), the author concludes that camphoric acid

must contain two asymmetric carbon atoms, provided the molecule is unsymmetrical.

The camphoric acids belong to the *cis*-type, and the isocamphoric acids to the *trans*-type.

The properties of the various camphoric acids, anhydrides, brom- and chlor-anhydrides are described in detail. J. J. S.

Constitution of Camphoric acid. By LUIGI BALBIANO (*Gazzetta*, 1896, **26**, i, 52—61).—The acid, $C_8H_{12}O_5$, prepared by Mahla and Tiemann (Abstr., 1895, i, 678) and by the author (Abstr., 1894, i, 614; 1895, i, 522) is considered by the German chemists to be a ketonic dicarboxylic acid of the constitution $COOH \cdot CHMe \cdot CMe_2 \cdot CO \cdot COOH$, and is stated by them to yield a bromophenylhydrazone melting at 161—162°. The author finds that in acetic acid solution the acid, $C_8H_{12}O_5$, reacts readily with parabromophenylhydrazine yielding an additive compound of the composition $C_{14}H_{18}BrN_2O_5$; it is a micro-crystalline, yellow powder melting with decomposition at 146—147°, and is a dibasic acid. On heating its aqueous solution neutralised with soda, or its alcoholic solution, hydrolysis occurs and a substance $C_{14}H_{17}BrN_2O_4$, is formed, having the composition of a bromophenylhydrazone of the acid, $C_8H_{12}O_5$; this crystallises in microscopic, yellow needles, melting and decomposing at 153—154°, and is a dibasic acid. Its calcium salt, $C_{14}H_{15}BrN_2O_4Ca \cdot 2H_2O$, is a sparingly soluble, white powder, which loses its water over sulphuric acid, and decomposes at 150°. The acid is not changed by boiling with baryta solution, or by heating in sealed tubes with hydrochloric acid; it is evident that it has not the properties of a hydrazone. The author, therefore, considers that the acid $C_8H_{12}O_5$ is not a ketonic acid, but has the constitution $COOH \cdot CH < \underset{O}{\overset{CMe_2}{\parallel}} > CMe \cdot COOH$; the additive product might then have the constitution



and should easily lose water yielding a pyrazolidine derivative.

W. J. P.

Sandarac Resin. By A. BALZER (*Arch. Pharm.*, 1896, **234**, 289—316).—Sandarac resin contains a very small amount of an ethereal oil and of a bitter substance, which can be obtained as a yellow powder, but consists chiefly of two acids, sandaracolic acid, the potassium salt of which is insoluble in concentrated potash, and callitric acid, the potassium salt of which is soluble. The former constitutes about 85, the latter about 10 per cent. of the crude resin. When submitted to distillation, the resin yields acetic acid, and a substance smelling like camphor.

Sandaracolic acid, $OMe \cdot C_{45}H_{81}O_3(OH) \cdot COOH$, is a white, crystalline powder, melting at 140°. The molecular weight was determined by the cryoscopic method in phenol solution. It yields a red solution with sulphuric acid, a sulphonic acid being formed which could not be obtained pure. The *silver salt* of sandaracolic acid has the formula $C_{45}H_{85}AgO_7$, and is a white powder. The *acetyl derivative* and the *benzoyl derivative* are brownish-yellow powders, which could not be

obtained crystalline, but yielded satisfactory numbers when analysed. The presence of a methoxy-group in the acid was proved by Zeisel's method. Nitric acid converts the acid into an oxidised product, $C_{40}H_{42}O_{13}$, picric acid being also formed together with oxalic acid, when concentrated nitric acid is used. When distilled with zinc dust, a number of aromatic substances are formed, benzene and toluene having been isolated from the product.

Callitrolic acid, $OH \cdot C_{64}H_{82}O_5 \cdot COOH$, forms colourless, prismatic crystals melting at 248° , and, like sandaracolic acid, is a monobasic hydroxy-acid. The *copper salt* crystallises from a mixture of alcohol and ether in plates melting at 185° ; the *acetyl derivative* is a light brown, amorphous powder.

These two acids afford a further confirmation of the generalisation made by Tschirch (Pringsheims' *Jahrbücher*, 1893, **25**, 379), that all the resin acids of the coniferæ are hydroxy-acids. A. H.

Luteolin. By JOSEF HERZIG (*Ber.*, 1896, **29**, 1013—1014; compare A. G. Perkin, *Trans.*, 1896, 206).—Luteolin is not identical with fisetin, $C_{15}H_{10}O_6$, for its acetyl derivative melts at 223 — 226° (Perkin, 213 — 215°), whilst acetylfisetin melts at 196 — 199° . Acetyluteolin gives the same numbers, on analysis, as tetracetylfisetin. The alkyl derivatives of luteolin have not yet been got white, as they should be if they are really tetralkyl derivatives, assuming luteolin to be analogous to fisetin; it is the trialkyl derivatives of fisetin that are yellow. The author thinks that phloroglucinol is really formed in addition to protocathechuic acid when luteolin is decomposed by aqueous alkalis; he recognised it by the pine-splinter test, which is more delicate than the ferric chloride test employed by Perkin. If this is so, luteolin is not closely related to fisetin, but rather to chrysin. [Compare further Perkin, *Trans.*, 1896, 799.]

C. F. B.

Pharmaceutical and Chemical Characteristics of Cubebs and the Piperaceous Fruits used for its Adulteration. By KARL PEINEMANN (*Arch. Pharm.*, 1896, **234**, 204—271).—Cubebs, a drug which has been known since the time of the Arabian physicians of the middle ages, was very largely used about 1880 in cases of catarrh, and, in the form of cigarettes, as a remedy for asthma, the result being that it rose very rapidly in price, and was very largely adulterated by the dealers. The various fruits, both piperaceous and belonging to other families, may be, for the most part, distinguished from the true cubebs simply by their external characteristics, whilst others resemble the genuine product so closely that a microscopic examination of a section of the fruit is necessary. A few of the substances employed for this purpose, however, belong to the same species as cubebs, and can only be distinguished by the fact that they do not contain cubebin, and therefore do not give a purple-red coloration with strong sulphuric acid. Cubebin does not occur in the perisperm only, as has hitherto been supposed, but also in the pericarp, and the same is true of the occurrence of piperine in black pepper. Piperaceous plants which contain cubebin or an allied compound do not, as a rule, contain any alkaloid, such as piperine, but one plant

has been found which is an exception to this. *Piper Lowong*, Bl., is found to contain 1·5 per cent. of piperine and 0·71 per cent. of a substance which closely resembles cubebin, but is isomeric with it, and is, therefore, termed *pseudocubebin*, $C_{20}H_{20}O_6$. This compound crystallises in long needles, melts at 122° , and in chloroform solution is dextrorotatory, whilst cubebin melts at 125° , and is lævorotatory. Pseudocubebin, moreover, has no taste, and gives a yellowish-brown coloration with sulphuric acid, whilst cubebin has a penetrating bitter taste, and is coloured a reddish-purple by sulphuric acid. The molecular formula was determined by the boiling point method in benzene solution. By oxidation with potassium permanganate, pseudocubebin is converted into piperonylic acid, in the same way as cubebin, but when fused with potash, it yields no solid product which could be isolated, whilst cubebin is thereby converted into protocatechuic and acetic acids. Bromine converts pseudocubebin into the *dibromo-compound*, which crystallises in silky needles melting at 177° . *Dinitropseudocubebin* crystallises in small, yellow needles, almost insoluble in acetic acid. The corresponding *dinitrocubebin* also forms small needles, melts at $182\cdot5^\circ$, and dissolves moderately freely in acetic acid. Pseudocubebin is not attacked by benzoic chloride or sodium ethoxide, and is converted into a brown resin by hydrochloric acid at 100° . Alcoholic hydrogen chloride, on the other hand, converts it into a white, amorphous powder, which could not be obtained pure.

The ethereal oil present in *Piper Lowong*, Bl., may be divided by fractionation into two parts; that which boils at the higher temperature contains a crystalline substance, which melts at 164° , and has the composition $C_{18}H_{20}O_2$.

The substance described as cubebin by various authors does not always appear to be the same compound. The molecular weight of some specimens corresponds with the formula $C_{20}H_{20}O_6$, whilst the molecular formula of others is $C_{40}H_{40}O_{12}$. The melting point, solubility, and even the colour reactions also vary, as do the products obtained by bromination and nitration.

A. H.

Proteacin [Leucodrin]. By OSWALD HESSE (*Annalen*, 1896, **290**, 314—317).—Proteacin is extracted by ether from the leaves of *Leucodendron concinnum*, and is the substance referred to by Beck as protexin, and by Merck as leucodrin; the latter name is now adopted by the author.

Leucodrin, $C_{18}H_{20}O_3$, crystallises in colourless, rhombic prisms, and melts at 212° , decomposing at higher temperatures; it is intensely bitter, and dissolves readily in hot water, being more sparingly soluble in cold; the aqueous solution, which is neutral, develops no coloration with ferric chloride. It dissolves in caustic soda, and after treatment with boiling, concentrated sulphuric acid, reduces Fehling's solution. The *triacetyl* derivative crystallises from alcohol.

M. O. F.

Sugar-bush (Protea Mellifera). By OSWALD HESSE (*Annalen*, 1896, **290**, 317—321).—*Protea mellifera* is a South African shrub which owes its colloquial name of sugar-bush to the sweet juice extracted from its blossoms; the syrup obtained on evaporating this

juice with ginger, finds application as a remedy for catarrh. The shrub has been erroneously regarded as the source of Beck's protexin; the leaves, however, yield a preparation which melts at 172° (compare foregoing abstract), whilst leucodrin melts at 212° . Extraction of the leaves, twigs, and blossoms with ether effects the isolation of two crystalline substances—a phenol and an acid; the former is quinol, whilst the acid stands in the same relation to homoprotocatechuic acid as that substance does to protocatechuic acid.

Proteaic acid, $C_6H_2Et(OH)_2 \cdot COOH$, separates from water in white crystals, which become yellow in air; it melts at 187° , carbonic anhydride being eliminated. Whilst indifferent towards Fehling's solution, the acid reduces silver nitrate; solutions of the alkali salts rapidly become dark brown, absorbing oxygen. The lead salt, $(C_6H_3O_4Pb)_2 \cdot PbO$, is a yellow, crystalline substance, which contains $1H_2O$; it loses water at 120° .
M. O. F.

Chlorophyll. IV. By EDWARD SCHUNCK and LEO MARCHLEWSKI (*Annalen*, 1896, **290**, 306—313).—A direct comparison of phylloporphyrin (Abstr., 1895, i, 297) with the hæmatoporphyrin of Nencki and Sieber indicates that the relationship between these substances is a close one, and the authors' investigation renders it probable that the latter colouring matter is dihydroxyphylloporphyrin. Nencki and Sieber ascribed to hæmatoporphyrin the formula $C_{16}H_{18}N_2O_3$, whilst phylloporphyrin most probably has the composition $C_{16}H_{18}N_2O$ (compare *loc. cit.*); in chemical properties, moreover, the substances are distinct, phylloporphyrin is insoluble in aqueous alkalis, but yields a crystalline zinc derivative, whilst hæmatoporphyrin dissolves readily in alkalis, but does not give rise to a zinc derivative, and has not been obtained in the crystalline condition. The most striking agreement between the compounds, however, lies in their characteristic absorption spectra, this point being clearly illustrated in the original paper by a plate representing the spectra of the two compounds dissolved in ether and in hydrochloric acid, and of the zinc derivatives in alcoholic solution.
M. O. F.

Action of Halogens on the Colouring Matter of the Kermes Berry (*Phytolacca decandra*, L.). By ALBERT HILGER and CARL MAI (*Chem. Centr.*, 1895, ii, 1083—1084; from *Forsch. Ber. Lebensm. Hyg.*, **2**, 343—346).—Chlorine and bromine readily decolorise the juice of kermes berries; iodine, however, has very little action. The authors have prepared a considerable quantity of the decolorised product by adding the juice, previously treated with hydrochloric acid, to a 10 per cent. solution of soda saturated with chlorine. The white, flocculent precipitate (5—6 grams from 8 kilos. of juice), on washing and drying, forms an amorphous, yellowish-grey powder, which is insoluble in water and ether, moderately soluble in aqueous alcohol, sparingly in acetone, chloroform, &c. The solution in potash turns brown after a time, and, on heating, yields chloroform. It is readily converted into acetyl or benzoyl derivatives, and also yields alkyl derivatives; dilute nitric acid dissolves it with evolution of nitrous fumes.

The colouring matter of red grapes and of bilberries is acted on by chlorine and bromine, and also by iodine. J. J. S.

Pyridineacetone Chloride. By DANIEL KNUTTEL (*Chem. Centr.*, 1895, ii, 895—896; from *Diss. Marburg*).—The author states that the melting point of the double compound obtained from pyridineacetone chloride and mercuric chloride is 120° (Dreser gives 119°). Copper and cadmium chlorides give no additive compounds. Pyridineacetone chloride, when distilled with soda, is decomposed, and yields pyridine. With hydroxylamine, it yields *pyridineacetoxime chloride*, which melts at 182 — 184° , its *platinochloride* at 204 — 205° , and its *aurochloride* at 144 — 145° ; the oxime, when heated with acetic chloride for five hours on the water bath, yields an *acetyl* derivative, the *platinochloride* of which melts at 195° to 197° and the *aurochloride* at 140 — 141° . Acetic anhydride, benzoic chloride and anhydride, and concentrated hydrochloric acid decompose the oxime. Sodium amalgam and acids, and also formamide, entirely decompose the oxime; moist silver oxide converts the oxime chloride into the free base.

Pyridineacetone chloride, in acetic acid solution, yields, with phenylhydrazine, a *phenylhydrazide*, which melts at 133 — 134° . Piperidine and chloracetone unite in benzene solution to form a compound already described by Störmer and Burkert; pyridine, apparently, does not unite with chloracetone. J. J. S.

β -Naphthylpiperidine and β -Naphthyl-2-pipecoline. By W. ROTH (*Ber.*, 1896, 29, 1175—1181; compare this vol., i, 253).— β -Naphthylpiperidine, $C_{10}H_7 \cdot C_5NH_{10}$ (Lellmann, *Abstr.*, 1890, 1003), was prepared by heating piperidine (1 mol.) with β -naphthol (1 mol.) for four hours at 250 — 260° in a sealed tube. It melts at 56° (corr.); the *hydrochloride*, *sulphate*, with $3H_2O$, and yellow *aurochloride*, with $4H_2O$, and *picrate* melt respectively at 214° , 105° , 131 — 132° , and 188° . It is reduced by sodium in boiling amylic alcoholic solution to *tetrahydro- β -naphthylpiperidine*, $\begin{array}{c} CH_2 \cdot CH_2 \cdot C \cdot CH \cdot C \cdot C_5NH_{10} \\ | \\ CH_2 \cdot CH_2 \cdot C \cdot CH \cdot CH \end{array}$; this is an oil boiling at 274 — 276° (corr.) under 749 mm., and at 190 — 196° (corr.) under 24 mm. pressure; its *hydrochloride*, *platinochloride*, with $3H_2O$, *aurochloride*, and *picrate* melt respectively at 210 — 211° , 156 — 159° , 135° , and 166° ; oxidation with permanganate converts it into adipic and oxalic acids.

β -Naphthyl-2-pipecoline, $C_{10}H_7 \cdot C_5NH_5Me$, was prepared in a similar manner from 2-pipecoline and β -naphthol. It was obtained as a yellowish oil, boiling at 186 — 190° (corr.) under 10 mm. pressure; the *platinochloride*, with $6H_2O$, and *picrate* melt respectively at 145° and 153 — 154° ; the *hydrochloride* and *aurochloride*, with $9H_2O$, were also prepared and analysed. C. F. B.

Ladenburg's "Isopipecoline." By WILHELM MARCKWALD (*Ber.*, 1896, 29, 1293—1296).—The author maintains his conclusion that "isopipecoline" is a mixture of *d*- and *l*-pipecoline (this vol., i, 253),

and shows that Ladenburg's argument (*ibid.*, 378) against it is fallacious.

C. F. B.

4-Nitro-, 1-Nitro-, 4-Amido-, and 1-Amido-quinoline. By ADOLPH CLAUS and EUGEN SETZER (*J. pr. Chem.*, 1896, [2], 53, 390—413).—Details of the best method for nitrating quinoline in order to obtain 1- and 4-nitroquinoline are given. The nitrate of the 4-derivative is so insoluble in nitric acid that it may be separated by this means from the accompanying isomeride. 1-Nitroquinoline forms no additive compound directly with alkylic haloïds. The *methiodide* of 4-nitroquinoline may be prepared by heating its components together; it crystallises in dark red prisms and needles, and melts and decomposes at 215°. 1-Nitroquinoline does not yield a bromo-derivative by the Claus-Collischon method, but 4-nitroquinoline yields 3'-bromo-4-nitroquinoline (m. p. 136°; Abstr., 1889, 728); neither nitroquinoline can be directly brominated.

4-Nitrocarbostyryl is prepared from 4-nitroquinoline by treating it with a solution of bleaching powder in the presence of boric acid, and decomposing the hypochlorous acid compound which separates by hot aqueous soda; on adding strong hydrochloric acid to the hot alkaline solution, 4-nitrocarbostyryl is liberated and separates on cooling. It crystallises from hot alcohol in golden-yellow, lustrous needles and laminæ, and melts at 304°; it is probably identical with the nitrocarbostyryl (m. p. 302°) prepared by Claus and Pollitz (Abstr., 1890, 521). No carbostyryl could be prepared from 1-nitroquinoline by the bleaching powder reaction (compare Abstr., 1891, 1218; 1888, 502).

2':4-Chloronitroquinoline is obtained when 4-nitrocarbostyryl is heated with phosphoric chloride; it crystallises in yellowish-green needles, and melts at 130°.

4-Amidocarbostyryl crystallises in long, silky, colourless needles, melts at 250°, and dissolves in hot water.

By methylating 4-nitrocarbostyryl, 4:1'-nitromethylquinolone is obtained; it melts at 165°, and is identical with Decker's compound (Abstr., 1892, 880).

1-Amidoquinoline melts at 70° (uncorr.), not 67° as heretofore stated; 4-amidoquinoline melts at 110°, and boils at 310°. By direct bromination, 1-amidoquinoline yields 2:4:1-dibromamidoquinoline (Abstr., 1894, 553), but bromo-1-amidoquinoline cannot be prepared in this manner; when, however, the acetyl-group is introduced into the amido-group the direct entry of one atom of bromine becomes possible. 1-Acetamidoquinoline is best prepared by adding the calculated quantity of acetic anhydride to a solution of 1-amidoquinoline in benzene and evaporating at the ordinary temperature in a current of air; it crystallises from alcohol in colourless, flattened needles, and melts at 103°. 4:1-Bromacetamidquinoline crystallises in long, silky, colourless needles, and melts at 140°; its orientation is settled by de-acetylisng it, when it yields 4:1-bromamidoquinoline (m. p. 104°; Abstr., 1890, 173; 1894, i, 54). The three homonuclear bromo-1-amidoquinolines are now known.

4-Amidoquinoline behaves like the 1-derivative towards bromine,

the direct action producing 1 : 3 : 4-dibromamidoquinoline, which has been already described (Abstr., 1895, i, 565). 4-Acetamidoquinoline crystallises in lustrous, colourless needles, and melts at 178°; by bromination it yields 4 : 1-acetamidobromoquinoline, which forms yellowish-tinted needles, melts at 250°, and gives rise to 1 : 4-brom-amidoquinoline (Abstr., 1893, i, 668) when de-acetylisied.

A. G. B.

Action of Chlorine on Hydroxyquinolines. III. Chlorhydroxy- α -quinolinequinone. By THEODOR ZINCKE and E. WINZHEIMER (*Annalen*, 1896, 290, 321—359; compare Abstr., 1891, 1249).—The authors have obtained from 2 : 3-chlorhydroxy-1 : 4-quinolinequinone (*loc. cit.*) a series of derivatives analogous with those obtained by Zincke and Gerland from chlorhydroxy- α -naphthaquinone (Abstr., 1888, 290, 1192, and 1198).

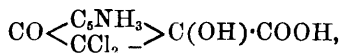
2 : 3-Chlorhydroxy-1 : 4-quinolinequinone is obtained from the product of chlorinating 3-hydroxyquinoline; this substance, tetrachloroketohydroquinoline, is reduced to dichlorohydroxyquinoline, which, on further chlorination, yields tetrachloroketoquinoline, this being converted into anilidotrichloroketoquinoline, and ultimately into monochloranilidoquinolinequinoneanilide, the final stage in the operation consisting in the hydrolysis of the last-named substance. The *sodium* derivative crystallises from water in dark red leaflets; the *acetyl* derivative separates from ether in slender, yellowish needles which melt and decompose at 176—177°. The *aniline* derivative crystallises from dilute acetic acid in microscopic, brick-red needles, which become colourless at 180°, and melt and decompose at 194°; the *oxime* is a yellow, amorphous powder, and dissolves in alkalis.

2 : 1 : 3 : 4-Chlorotrihydroxyquinoline, obtained by reducing the quinone with stannous chloride, crystallises in silvery leaflets containing 1H₂O; it melts at 225°, and in the anhydrous condition is a brick-red powder. The *hydrochloride* crystallises in slender, yellow needles, and melts without undergoing decomposition.

2-Dichloro-1 : 3 : 4-triketohydroquinoline hydrate is produced when chlorine is passed into a solution of chlorhydroxyquinolinequinone in 10 volumes of glacial acetic acid; it crystallises from a mixture of benzene and acetone in colourless, slender needles or aggregates of prisms, which weather rapidly. The substance melts at about 100°, effervescing vigorously, and yielding chlorhydroxyquinolinequinone; in consequence of this behaviour, the compound has not been obtained in the anhydrous state. The *hydrochloride*, C₉H₃Cl₂NO₃.HCl + 4H₂O, is a colourless, crystalline powder, and yields the hydrochloride of chlorhydroxyquinolinequinone when heated at 110°.

β -Chloro- α -hydroxypyrrindone, C₈NH₃< $\begin{smallmatrix} \text{CO} \\ \text{C(OH)} \end{smallmatrix}$ >CCl, is obtained by treating the foregoing ketone with boiling water, and crystallises from that solvent in long, slender needles or lustrous, red prisms; it becomes dark and chars when heated, but does not melt. The *sodium* derivative crystallises in bright orange leaflets, and the *potassium* derivative forms silky, orange needles; the *anilide* crystallises from alcohol in small, orange needles melting at 162—163°, and dissolves in alkalis.

β-Dichloro-αγ-ketopyrhydrindenecarboxylic acid,



is an intermediate compound in the production of the foregoing substance, and is obtained by dissolving dichlorotriketohydroquinoline hydrate or its hydrochloride in 10 per cent. soda, acidifying without delay, and agitating several times with ether; it crystallises from hot, concentrated hydrochloric acid on adding a small quantity of water, and melts at 105—110° with vigorous effervescence. The *methylic* salt separates from ether or benzene in colourless, transparent, monoclinic crystals, and melts and decomposes at 171°.

β-Dichloro-αγ-diketopyrhydrindene, $\text{C}_6\text{NH}_3 < \begin{smallmatrix} \text{CO} \\ \text{CO} \end{smallmatrix} > \text{CCl}_2$, is obtained by passing chlorine into concentrated hydrochloric and glacial acetic acids containing chlorhydroxypyridone in suspension; the *hydrochloride* separates from this liquid in transparent prisms, and yields the diketone on treatment with water. The substance is readily soluble, and crystallises from dilute alcohol in white needles melting at 106—107°; the *platinochloride* forms golden-yellow prisms, and melts at 200°.

β-Dichloracetopicolinic acid, $\text{COOH} \cdot \text{C}_6\text{NH}_3 \cdot \text{CO} \cdot \text{CHCl}_2$, is prepared by suspending the hydrochloride of dichlorodiketopyrhydrindene in water, and slowly adding the liquid to excess of caustic soda; the product is obtained on acidifying the liquid, and crystallises from glacial acetic acid in lustrous, brownish prisms, which melt and effervesce at 151°. Hot, fuming sulphuric acid converts it into the lactone of *β-dichloroxyvinylpicolinic acid*, $\text{CO} < \begin{smallmatrix} \text{C}_6\text{NH}_3 \\ \text{O} \end{smallmatrix} > \text{C} \cdot \text{CCl}_2$, which crystallises from alcohol in long, slender, white needles, and melts at 135—136°.

β-Trichloracetopicolinic acid, $\text{CCl}_3 \cdot \text{CO} \cdot \text{C}_6\text{NH}_3 \cdot \text{COOH}$, is obtained on chlorinating dichloracetopicolinic acid dissolved in sodium carbonate, and by the action of bleaching powder on chlorhydroxyquinoline-quinone or the triketo-compound; it crystallises from hot, dilute hydrochloric acid in colourless, lustrous leaflets, and melts and decomposes at 174°. Caustic soda resolves the substance into chloroform and quinolinic acid.

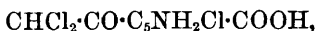
The lactone of *β-hydroxymethylpicolinic acid*, $\text{C}_6\text{NH}_3 < \begin{smallmatrix} \text{CH}_2 \\ \text{CO} \end{smallmatrix} > \text{O}$, is produced on heating the foregoing lactone or dichloracetopicolinic acid in sealed tubes with concentrated hydrochloric acid for three hours at 165°, carbonic anhydride being eliminated; it crystallises from methylic alcohol in long, colourless, lustrous needles having the appearance of leaflets, and melts at 161°. The *platinochloride* crystallises in lustrous, golden-yellow prisms, and contains $2\text{H}_2\text{O}$; barium hydroxide converts the lactone into the *barium* salt, which crystallises from water in brownish prisms containing $2\text{H}_2\text{O}$.

β-Methylpicolinic acid, $\text{C}_6\text{NH}_3\text{Me} \cdot \text{COOH}$ [Me : COOH = 3 : 2], is obtained by reducing the foregoing lactone with hydriodic acid, and crystallises from alcohol in nodules of yellowish prisms, which melt

at 111°. The *hydrochloride* forms lustrous, white leaflets, and the *platinochloride* crystallises from absolute alcohol in small, yellow prisms, and melts at 192°; the crystals contain 2H₂O, which is lost at 100°.

β-Dichloro-αγ-diketochloropyrhydrindone, $C_5NH_2Cl \begin{smallmatrix} CO \\ \diagup \diagdown \\ CO \end{smallmatrix} CCl_2$, arises from chlorohydroxypyrindone by chlorination in absence of hydrochloric acid; it crystallises from glacial acetic acid on adding a small quantity of water to the solution, and melts at 100°. Reduction with stannous chloride converts it into *chlorhydroxychloropyrindone*, $C_5NH_2Cl \begin{smallmatrix} CO \\ \diagup \diagdown \\ C(OH) \end{smallmatrix} CCl$, which separates from glacial acetic acid in the form of a bright red, crystalline powder; it darkens at 150°, sinters at 170°, melts and decomposes at 180°.

Dichloracetochloropyridinecarboxylic acid,



is obtained by the action of soda on the foregoing diketo-compound; it crystallises from benzene in colourless, microscopic needles, and melts to a red liquid at 148°. M. O. F.

Action of Chlorine on Hydroxyquinolines. IV. Dichloro-β-quinolinequinone. By THEODOR ZINCKE and K. WIEDERHOLD (*Annalen*, 1896, **290**, 359—382; compare the foregoing abstract).—1 : 2-Dichloro-3 : 4-quinolinequinone (*dichloro-β-quinolinequinone*) is readily obtained by the action of chlorine on 3 : 4-hydroxyamidoquinoline in glacial acetic acid, and crystallises from alcohol in lustrous, yellow leaflets melting at 180°. The *hydrochloride* is a bright yellow, crystalline powder containing 1H₂O; it melts and decomposes at 199—200°.

1 : 2 : 3 : 4-Dichlorodihydroxyquinoline (*dichloro-β-quinolinequinol*) is obtained by reducing the quinone in alcoholic solution with stannous chloride; it is a red powder which begins to sublime and decompose at 150°. The *hydrochloride* crystallises in slender, yellow needles containing 1H₂O, and melts and decomposes at 170°.

Aniline converts dichloro-β-quinolinequinone into 2 : 3-chlorhydroxy-4 : 1-quinolinequinoneanilide, already described by Zincke and Müller (*Abstr.*, 1891, 1251); this melts at 175°, and not at 195°. The *paratoluidide* crystallises from alcohol or benzene in long, dark red needles, and melts at 178—180°; hydrolysis converts it and the anilide into chlorhydroxy-α-quinolinequinone (foregoing abstract).

αβ-Dichloropyrindone, $C_5NH_2 \begin{smallmatrix} CO \\ \diagup \diagdown \\ CCl \end{smallmatrix} CCl$, is obtained by suspending dichloro-β-quinolinequinone or its hydrochloride in water, and adding the liquid to ice-cold caustic soda solution containing sodium peroxide; it crystallises from methylic alcohol in long, slender, lustrous needles, and melts at 112°. It volatilises at higher temperatures, and is also volatile in an atmosphere of steam. Aniline converts it into α-anilido-β-chloropyrindone (m. p. 162—163°), described in the foregoing abstract.

Tetrachloropyrhydrindone, $C_5NH_3 \langle \begin{smallmatrix} CO- \\ CCl_2 \end{smallmatrix} \rangle CCl_2$, is produced by chlorinating $\alpha\beta$ -dichloropyrindone in chloroform. Caustic soda converts it into *trichlorovinylpyridinecarboxylic acid*, $CCl_2 \cdot CCl \cdot C_5NH_3 \cdot COOH$, which crystallises from benzene in greyish needles, and melts at $153-154^\circ$.

Dichlorovinylpyridinecarboxylic acid, $CHCl \cdot CCl \cdot C_5NH_3 \cdot COOH$, is obtained by the action of dilute soda on $\alpha\beta$ -dichloropyrindone: it crystallises from benzene in needles, and melts at 139° .

1 : 2-*Dichloroquinolinephenazine*, $CCl \langle \begin{smallmatrix} C_5NH_3 \cdot C:N \\ CCl - C:N \end{smallmatrix} \rangle C_6H_4$, is obtained on adding orthophenylenediamine dissolved in glacial acetic acid to a solution of dichloro- β -quinolinequinone in methylic alcohol; it crystallises from alcohol, and melts at $239-240^\circ$.

2 : 1-*Chlorhydroxyquinolinephenazine*, $OH \cdot C \langle \begin{smallmatrix} C_5NH_3 \cdot C:N \\ CCl - C:N \end{smallmatrix} \rangle C_6H_4$, arises from treatment of chlorhydroxy- α -quinolinequinone with orthophenylenediamine; it crystallises in lustrous, yellow needles, and melts above 200° . The *hydrochloride* is a carmine substance, and the *sodium* derivative is sparingly soluble in water. On suspending the eurhodole in glacial acetic acid, and adding a few drops of concentrated nitric acid to the hot liquid, 1 : 2-*diketquinolinephenazine hydrate*, $CO \langle \begin{smallmatrix} C_5NH_3 \cdot C:N \\ CO - C:N \end{smallmatrix} \rangle C_6H_4 \cdot H_2O$, is produced; it separates from glacial acetic acid as a yellow, crystalline powder, and melts above 270° . Orthophenylenediamine converts it into a yellowish-white compound which crystallises from alcohol in leaflets; this is probably a diphenazine derivative.

M. O. F.

Iodisoquinoline; the two isomeric Iodophthalic acids. By ALBERT EDINGER (*J. pr. Chem.*, 1896, [2], 53, 375-389; compare Abstr., 1895, i, 300).— α -*Iodisoquinoline* is prepared by diazotising α -amido-isoquinoline and immediately dropping the diazotised solution into a concentrated solution of potassium iodide; after 12 hours the solution is made strongly alkaline and distilled in steam. It sublimes at 100° in lustrous, white needles, melts at 98° , and is freely soluble in alcohol, ether, acetone, benzene, chloroform, &c., but only sparingly in hot water; it is a strong, tertiary base; the *methiodide* is anhydrous, and melts at 306° ; the *platinochloride* decomposes at 298° ; the *picrate* is anhydrous, and melts at 224° ; the *dichromate* is described.

α -*Iodophthalimide* is obtained by oxidising a neutral solution of α -iodisoquinoline sulphate with potassium permanganate. It crystallises from hot water in white needles, melts at 238° , and may be sublimed. For the identification of this compound, it was prepared synthetically from phthalic anhydride, this being first converted into ethylic hydrogen α -nitrophthalate by Miller's method (Abstr., 1882, 404). The author notes that ethylic hydrogen α -nitrophthalate crystallises with $2\frac{1}{2}H_2O$, and melts in this water at 50° , the anhydrous compound melting at 110° . Ethylic β -nitrophthalate melts at 34° .

α -Nitrophthalic acid was diazotised and converted into the iodo-acid by Bernthsen's method (Abstr., 1886, 363). The α -iodophthalic anhydride prepared in this way melted at 153° , and when heated in ammonia, yielded an imide which melted at 238° . α -Iodophthalic acid crystallises with $3\text{H}_2\text{O}$, and melts at 206° . The same acid, anhydride and imide, were prepared from diethylic α -iodophthalate (m. p. 70°). Potassium α -iodophthalate, with $3\text{H}_2\text{O}$, and the barium, silver, and copper, with $2\frac{1}{2}\text{H}_2\text{O}$, salts are described.

β -Iodophthalic acid was prepared by reducing and diazotising (in hydriodic acid solution) the normal β -ethylic salt obtained by Miller's method (*loc. cit.*), and hydrolysing the product. It was found to crystallise with $1\frac{1}{2}\text{H}_2\text{O}$, and to melt at 182° . The imide melts at 222 – 224° , and the anhydride at 123° . The acid was also prepared by oxidising barium β -iodo-1'- and β -iodo-4'-naphthalenesulphonate with potassium permanganate. The normal copper, with $3\text{H}_2\text{O}$, silver, potassium, and barium salts are described.

The α - and β -acids may be separated by means of their barium salts, that of the α -acid being the more soluble. The α -acid yields the ethylic hydrogen salt when treated with alcoholic hydrogen chloride; whilst the β -acid yields the normal ethylic salt; compare the behaviour of the nitro-acids (Miller's method, *loc. cit.*).

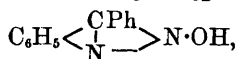
A. G. B.

A remarkable Formation of Acridone. By AMÉ PICTET and A. HUBERT (*Ber.*, 1896, 29, 1189–1191).—When salicylanilide, $\text{C}_6\text{H}_5\cdot\text{NH}\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{OH}$, is distilled, the main product, which remains in the carbonaceous residue, is not phenanthridone, but acridone, $\text{C}_6\text{H}_4\langle\begin{smallmatrix} \text{NH} \\ \text{CO} \end{smallmatrix}\rangle\text{C}_6\text{H}_4$ (compare Abstr., 1892, 1086). The anilide must have first undergone a molecular transformation into phenylanthranilic acid, $\text{COOH}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{C}_6\text{H}_5$, and it is evidence in favour of this that diphenylamine was found in the distillate. Salicyl-2-toluidide and 4-toluide behave in a similar manner, yielding 2-methylacridone and 4-methylacridone respectively (Abstr., 1894, i, 530). C. F. B.

Indazole Derivatives. By KARL AUWERS (*Ber.*, 1896, 29, 1255–1271).—The preparation of indazole derivatives, $\text{C}_6\text{H}_4\langle\begin{smallmatrix} -\text{CR} \\ \text{N}^+\text{Ac} \end{smallmatrix}\rangle\text{N}$, by the action of glacial acetic acid and acetic anhydride on the oximes of aromatic orthoamidoketones has been described by Auwers and Meyenburg (Abstr., 1891, 1375). Bischler has suggested (Abstr., 1893, i, 609) that the acetyl group participates in the reaction, and that the compounds are isindazole derivatives, $\text{C}_6\text{H}_4\langle\begin{smallmatrix} \text{CR}=\text{N} \\ \text{N}^+\text{CMe} \end{smallmatrix}\rangle\text{O}$, analogous to Tiemann's azoximes, $\text{RC}\langle\begin{smallmatrix} \text{N}\cdot\text{O} \\ \text{N}^+\text{CR} \end{smallmatrix}\rangle$; in general properties, the compounds exhibit marked differences, the former are volatile with steam, unstable towards alkali, and are strongly basic; whilst the latter are neutral, extremely readily volatile, and very stable towards both alkalis and acids.

With A. R. EWING.—1'-Acetylindazole, $C_6H_4<\overset{CH}{N_{Ac}}>N$, prepared from orthamidobenzaldoxime, crystallises in slender, almost colourless needles, with an indazole-like smell, gives a crystalline salt with mercuric chloride, and regenerates the oxime when treated with alkali at the ordinary temperature. The melting point of acetylorthamidobenzophenone was previously stated to be 72° , although Bischler and Barad (*loc. cit.*) state that it melts at $88.5-89^\circ$; a substance melting at this temperature was obtained in small quantity; further purification failed to change the melting point of the chief product, but subsequent preparations all melted at $88-89^\circ$. 1' : 3'-Acetylphenylindazole melts at 185° , and has been previously described; the acetate crystallises in prisms, and is quickly dissociated when boiled with water. By the action of highly dilute alcoholic soda on the isindazole, orthacetamidobenzophenoneoxime, $NHAc \cdot C_6H_4 \cdot CPh \cdot N \cdot OH$, is formed; it crystallises in lustrous plates, melts at about 180° , and yields a diacetyl derivative. When further treated with soda, both the isindazole and the monacetylloxime yield an orthamidobenzophenone oxime melting at $125-126^\circ$ (the melting point was previously stated to be $123-125^\circ$); it is stereoisomeric with the ordinary compound (m. p. 156°) into which both it and the isindazole are converted by prolonged boiling with soda; the reverse change occurs if the oxime of higher melting point is heated with absolute alcohol during several hours at $160-170^\circ$.

With A. SONDHEIMER.—2' : 3'-Hydroxyphenylindazole,



first noticed by Ewing, is prepared from orthamidobenzophenone by means of the diazo-reaction; it crystallises from water in slender, colourless, lustrous plates; from benzene in highly lustrous, pale yellow prisms, and melts at $125-126^\circ$. The purified compound is stable, but the presence of foreign matter causes rapid decomposition, especially on exposure to light. When boiled with water, benzophenone is produced in small quantity; distillation under reduced pressure also regenerates benzophenone, and nitrogen is evolved. Under conditions fully described in the original paper, the yield of indazole is 70 per cent. of the theoretical. The mercurichloride and silver nitrate crystallise from water in colourless needles. Hydrogen chloride in ethereal solution, benzoic chloride, picric acid, acetic anhydride, and phenylic cyanate are without action on the indazole, whilst acetic chloride decomposes it completely; it is oxidised by Fehling's solution, yielding a yellowish-red oil.

Isohydroxyphenylindazole, $C_{13}H_{10}N_2O$, is formed together with benzophenone (10 per cent.) by the action of dilute soda on the hydroxy-derivative; it crystallises in pearly, lustrous plates or needles melting at 212° . It is soluble in alkalis and in concentrated acids, and is reprecipitated from the latter on dilution; it may be crystallised from dilute hydrochloric acid. Attempts to reduce it have been unsuccessful. The yield is 50 per cent. of the theoretical; the molecular weight was determined by means of the cryoscopic method. The

acetyl derivative crystallises in long, colourless needles melting at 90—91°.

3-Phenylindazole, $C_6H_4<\underset{N}{\overset{CPh}{|}}>NH$, is formed in small quantity, along with the hydroxyphenylindazole, or by the reduction of the latter with zinc dust in alkaline or acid solution, but the best results are obtained by the use of stannous chloride; it crystallises in long, lustrous needles, melts at 107—108°, resolidifies at 109—110°, and melts again at 115—116°; the form having the higher melting point crystallises from light petroleum in highly lustrous prisms, and is reconverted into the first modification by heating above its melting point.

From solution, either form is deposited by the introduction of a crystal of the desired modification. The compound crystallises from soda in needles; when distilled under the ordinary pressure benzaldehyde is formed in traces. The yield is 85—90 per cent. of the theoretical. The mercuric and silver derivatives crystallise in needles; the sulphate is deposited in silky, lustrous needles; the hydrochloride, $C_{13}H_{10}N_2.HCl$, is crystalline and pulverulent; both salts are decomposed by water or soda, the modification of the indazole of lower melting point being regenerated. The picrate crystallises in dark yellow, lustrous rhomboids which effloresce on exposure to air. The nitroso-derivative is yellow, unstable in air, and difficult to purify; it softens at 70—80°. 2':3'-Acetylphenylindazole, $C_6H_4<\underset{N}{\overset{CPh}{|}}>NAc$, prepared

by the action of acetic anhydride on either modification of phenylindazole, crystallises in needles melting at 69—70°; with alkali, the modification of phenylindazole having lower melting point is regenerated. The constitution of these indazole derivatives cannot be regarded as definitely proved, and the subject is being further investigated. J. B. T.

The Pyrazolone Series. By SIEGFRIED RUHEMANN (*Ber.*, 1896, 29, 1016—1018).—Methylchloroform does not react with ethylic sodiomalonate, as chloroform itself does, to form ethylic dicarboxylglutaconate. Ethylic trichloracetate reacts, but the product is the same as when chloroform is employed.

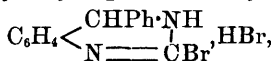
1:4-Dimethylpyrazolone-4-carboxylic acid, $\begin{matrix} NMe \cdot CO \\ | \\ N = CH \end{matrix} > CMe \cdot COOEt$, like the 1:4-phenylmethyl acid, is much more stable than the unsubstituted acid; it loses carbonic anhydride, however, at its melting point, 222°. C. F. B.

A Compound containing a Ring of Eight Atoms. By A. SONDHEIMER (*Ber.*, 1896, 29, 1272—1275).—Anhydrodiorthamidobenzophenone or diphenylphenhomazine, $C_6H_4<\underset{N}{\overset{CPh:N}{|}}>C_6H_4$, is prepared by heating orthamidobenzophenone hydrochloride between watch glasses at about 130°; the product is dissolved in ether, and the ketone separated by means of hydrochloric acid; it is deposited from light petroleum in yellow crystals, from glacial acetic acid and alcohol in fatty, lustrous plates, and melts at 190°, subliming at

higher temperatures. It is stable towards alkalis, dilute acids, and reducing agents; when heated with concentrated sulphuric acid at 160°, orthamidobenzophenone is quantitatively regenerated. Cryoscopic molecular weight determinations agree with the above formula. The yield of the azine is 30 per cent. of the theoretical, and some benzaldehyde is also formed; by friction, the azine becomes highly electrified, so that it is powdered with difficulty, the best way being to mix it with finely divided glass. J. B. T.

Quinazoline Compounds. By SIEGMUND GABRIEL and ROBERT STELZNER (*Ber.*, 1896, **29**, 1300—1316).—Orthamidobenzhydrol, $\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CHPh} \cdot \text{OH}$, does not react quite in the same way as orthamidobenzyl alcohol, $\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{OH}$ (*Abstr.*, 1895, i, 190, 432). Unlike the latter, it yields a crystallised thiotetrahydroquinazoline with thiocyanic acid, whilst it does not yield a carbamide with cyanic acid; it forms the anhydride of such a carbamide, however, when heated with carbamide itself, but this anhydride has the constitution $\text{C}_6\text{H}_4 < \begin{smallmatrix} \text{CHPh} \cdot \text{NH} \\ \text{NH} - \text{CO} \end{smallmatrix}$, whereas the anhydride of the carbamide from orthamidobenzyl alcohol has the constitution $\text{C}_6\text{H}_4 < \begin{smallmatrix} \text{CH}_2 \cdot \text{O} \\ \text{NH} \cdot \text{C} \cdot \text{NH} \end{smallmatrix}$ or $\text{C}_6\text{H}_4 < \begin{smallmatrix} \text{CH}_2 \cdot \text{O} \\ \text{N} = \text{C} \cdot \text{NH}_2 \end{smallmatrix}$ (Paal and Vanvolxem, *Abstr.*, 1894, i, 621).

Orthamidobenzhydrol was prepared by reducing orthamidobenzophenone with sodium amalgam in warm, aqueous alcoholic solution; it melts at 120°, its *acetyl derivative* at 118°. When warmed with dilute thiocyanic acid or a mixture of normal potassium thiocyanate solution with hydrochloric acid, it yields 4'-phenylthiotetrahydroquinazoline, $\text{C}_6\text{H}_4 < \begin{smallmatrix} \text{CHPh} \cdot \text{NH} \\ \text{NH} - \text{CS} \end{smallmatrix}$, melting at 230°. This can be reduced by sodium in alcoholic solution to 4'-phenyltetrahydroquinazoline, $\text{C}_6\text{H}_4 < \begin{smallmatrix} \text{CHPh} \cdot \text{NH} \\ \text{NH} - \text{CH}_2 \end{smallmatrix}$, the *hydrochloride* of which begins to decompose at about 200°. When suspended in acetic acid and brominated, it yields 2':4'-bromophenyldihydroquinazoline hydrobromide,



which turns brown at 200°, and melts and decomposes at 273—274°; the bromo-base itself melts at 165°, and, when boiled with excess of aqueous sodium carbonate, yields 4'-phenyltetrahydro-2'-quinazalone, $\text{C}_6\text{H}_4 < \begin{smallmatrix} \text{CHPh} \cdot \text{NH} \\ \text{NH} - \text{CO} \end{smallmatrix}$, which melts at 193° (the *acetate* at 132—133°), and is also formed when orthamidobenzhydrol is heated with carbamide at 175°. If orthamidobenzophenone is heated with carbamide at 195°, yellow 4'-phenylquinazolone (4'-phenyl-2'-ketodihydroquinazoline), $\text{C}_6\text{H}_4 < \begin{smallmatrix} \text{CPh} \cdot \text{N} \\ \text{NH} \cdot \text{CO} \end{smallmatrix}$, melting at 250—251°, is formed. This, when boiled with phosphoric oxychloride and pentachloride, yields

yellow 2'-chloro-4'-phenylquinazoline, $C_6H_4 < \begin{smallmatrix} CPh:N \\ N=CCl \end{smallmatrix}$, which melts at 113° , and is reduced by boiling with hydriodic acid and phosphorus to 4'-phenyldihydroquinazoline, $C_6H_4 < \begin{smallmatrix} CHPh:NH \\ N=CH \end{smallmatrix}$, melting at $165\text{--}166^\circ$.

The latter is also obtained by reducing the above mentioned bromo-base with hydriodic acid and phosphorus at $180\text{--}190^\circ$; its hydrochloride, orange platinochloride, yellow aurochloride, yellow picrate, and yellow nitroso-derivative melt at $242\text{--}243^\circ$, 234° , $181\text{--}182^\circ$, $213\text{--}214^\circ$, and 131° respectively.

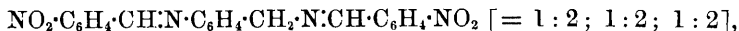
Quinazolone (2'-ketodihydroquinazoline), $C_6H_4 < \begin{smallmatrix} CH:N \\ NH:CO \end{smallmatrix}$ (Abstr., 1895, i, 433), when boiled with phosphorus pentachloride and oxychloride, yields yellowish 2'-chloroquinazoline, $C_6H_4 < \begin{smallmatrix} CH:N \\ N=CCl \end{smallmatrix}$, which melts at 108° ; this is reduced by hydriodic acid to dihydroquinazoline, $C_6H_4 < \begin{smallmatrix} CH_2:NH \\ N=CH \end{smallmatrix}$, melting at $126\text{--}127^\circ$. With phosphorus pentachloride and oxychloride, 4'-hydroxyquinazoline (4'-ketodihydroquinazoline), $C_6H_4 < \begin{smallmatrix} C(OH):N \\ N=CH \end{smallmatrix}$ or $C_6H_4 < \begin{smallmatrix} CO:NH \\ N=CH \end{smallmatrix}$ (von Niementowski, Abstr., 1895, i, 571) yields 4'-chloroquinazoline, $C_6H_4 < \begin{smallmatrix} CCl:N \\ N=CH \end{smallmatrix}$, which melts at 96° , and has a great tendency to go back into the hydroxy-compound.

Orthocyanodiphenylmethane, $CN \cdot C_6H_4 \cdot CH_2Ph$ (Cassirerer, Abstr., 1893, i, 16) can be converted by chlorination at $150\text{--}160^\circ$ into α -chlororthocyanodiphenylmethane, $CN \cdot C_6H_4 \cdot CHPhCl$. This is an oil, which, when heated with hydrochloric acid at 150° , yields phthalimide, and, when boiled with aqueous-alcoholic potassium cyanide, does not yield dicyanodiphenylmethane, but cyanohydroxydiphenylmethane, $CN \cdot C_6H_4 \cdot CHPh \cdot OH$, which is also an oil. C. F. B.

Orthamidobenzylamines. III. By MAX BUSCH [and KARL DIETZ] (*J. pr. Chem.*, 1896, [2], 53, 414—427; compare Abstr., 1894, i, 146; 1895, i, 306, 307).—Formaldehyde condenses with orthamidobenzylamine to form tetrahydroquinazoline; with orthamidobenzylaniline to form 3'-phenyltetrahydroquinazoline; with orthamidobenzylparatoluidine to form 3'-paratolyltetrahydroquinazoline (long, white needles, m. p. 127°); with orthamidobenzylorthotoluidine to form 3'-orthotolyltetrahydroquinazoline (white crystals, m. p. 140°); with orthamidobenzylorthanisidine to form 3'-orthanisyltetrahydroquinazoline, which forms colourless crystals, melts at $141\text{--}142^\circ$, and dissolves in light petroleum, benzene, and chloroform, but less readily in ether or alcohol. These condensation products are decomposed into their parent compounds by acids.

Orthamidobenzylamine condenses with metanitrobenzaldehyde to form 2'-metanitrophenyltetrahydroquinazoline, which crystallises in pale yellow, transparent prisms, melts at $84\text{--}85^\circ$, and dissolves freely in

the usual organic solvents; dilute mineral acids decompose it into the base and aldehyde. With orthonitrobenzaldehyde, orthamidobenzylamine condenses to form a *compound*, probably



which crystallises in lustrous, yellow prisms, softens at 125° , and melts at 128° : it is freely soluble in benzene and chloroform, sparingly in ether and alcohol, and almost insoluble in light petroleum.

2'-*Parahydroxyphenyltetrahydroquinazoline* is the product of the condensation of parahydroxybenzaldehyde with orthamidobenzylamine; it crystallises from dilute alcohol in thick, nearly colourless needles, melts at $167\text{--}168^\circ$, and is scarcely at all soluble in light petroleum, sparingly in benzene, chloroform, and hot water, freely in alcohol.

The *compound* $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{OH}$ is formed from orthamidobenzylamine and salicylaldehyde; it crystallises in transparent yellow prisms and silky needles, melts at $107\text{--}108^\circ$, and dissolves freely in alcohol and benzene, sparingly in ether and light petroleum.

Orthamidobenzylphenylhydrazine and formaldehyde condense to form a dimethylene *compound*, $\text{CH}_2\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{NPh}\cdot\text{N}\cdot\text{CH}_2$, which crystallises in reddish prisms and needles, melts at 84° , and dissolves freely in benzene, less freely in alcohol and ether, and sparingly in light petroleum; with dilute sulphuric acid it gives formaldehyde.

A. G. B.

Relationship of Indulines to Safranines. By FRIEDRICH KEHRMANN (*Annalen*, 1896, **290**, 247—306; compare Abstr., 1895, i, 148 and 527, also Fischer and Hepp, Abstr., 1895, i, 608, and this vol., i, 50).—The author's experiments lead him to the conclusion that the indulines and safranines represent the amido- and hydroxy-derivatives of one large group of azonium bases; those bases which are not substituted exist in the form of hydrates, in this respect resembling those derivatives which, by reason of the position of the substituents, have not the property of forming paraquinonoid anhydrides (indulines or indones). The substituted azonium bases, on the other hand, which have the amido- or hydroxy-group in a favourable position, although sometimes occurring as hydrates, exhibit a tendency to lose water, as in the case of rosinduline, aposafranine, and pheno-safranine. The indulines and indones arising in this manner, however, yield salts identical with those of the respective azonium hydrates, molecular rearrangement to the orthoquinonoid azonium type occurring simultaneously with salt formation (compare Abstr., 1895, i, 527).

With M. HERTZ.—When acetamidonaphthaquinone and phenyl-orthophenylenediamine hydrochloride are heated together in alcohol, condensation takes place, and two isomeric hydrochlorides are produced (Abstr., 1895, i, 148); these may be separated by fractional crystallisation, or by the application of ammonium carbonate. The less soluble hydrochloride, $\text{C}_{24}\text{H}_{17}\text{N}_3\text{O}\cdot\text{HCl}$, crystallises from alcohol or hot water in red needles with green iridescence, the alcoholic solution

being yellowish-red, and exhibiting greenish-yellow fluorescence. This modification decomposes at 290° , whilst 260° is the point at which the more soluble hydrochloride decomposes; the latter crystallises from alcohol in dark, brownish-red plates having a blue lustre, and the solution, which is dark red, does not exhibit fluorescence. The former modification yields rosinduline hydrochloride on elimination of the acetyl group, the same change in the more soluble modification giving rise to an isomeric rosinduline hydrochloride. Both forms of the original salt yield a bright red, crystalline *platinochloride*, and the *hydrogen sulphate* of the more soluble modification crystallises in brownish-red, lustrous needles; the behaviour of the isomerides towards various agents is described in the original paper.

Acetylosinduline, $\text{N} \begin{smallmatrix} \text{—} \\ \text{N} \end{smallmatrix} \text{Ph} > \text{C}_6\text{H}_4$, is obtained by adding aqueous alkali or alkali carbonates to a solution of the less soluble hydrochloride, and crystallises from a mixture of alcohol and benzene in small, dark red plates with golden lustre; it is also formed when rosinduline hydrochloride is heated with sodium acetate and acetic anhydride.

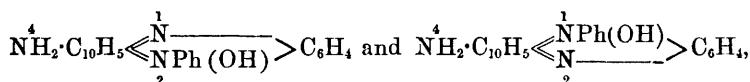
Rosinduline hydrate is produced by adding ammonia in slight excess to a cold dilute solution of the hydrochloride, and treating the liquid with a few drops of ether, in order to induce crystallisation; it is important that the ammonia employed should be free from carbonate, as, in presence of moisture, the base absorbs carbonic anhydride with great readiness. At $100\text{--}110^{\circ}$ the hydrate loses H_2O , and is converted into the anhydrous form of rosinduline, described already by Fischer and Hepp; the hydrate melts at $185\text{--}187^{\circ}$, the anhydride at 195° , and, whilst the latter dissolves readily in ether and benzene, the hydrate is sparingly soluble in them.

Rosinduline carbonate, $(\text{C}_{22}\text{H}_{16}\text{N}_3)_2\text{CO}_3$, is obtained in short, dark red, prismatic crystals, containing $4\text{H}_2\text{O}$; it is sparingly soluble in cold water, but dissolves readily at $40\text{--}50^{\circ}$, and, on boiling the solution, carbonic anhydride is evolved, and the anhydrous base crystallises from the almost colourless liquid.

The property of forming carbonates is exhibited by many other feeble azonium bases, and the author describes experiments with the oxidation products of alkylated orthodiamines, which Fischer and Heiler (Abstr., 1893, i, 266) regard as induline derivatives. Thus, the oxidation product of phenylorthophenylenediamine, which is isomeric with anilineaposafranine (Abstr., 1895, i, 528), absorbs no trace of carbonic anhydride in the crystalline condition or in aqueous solution, but, on saturating the ethereal solution with water and leading a stream of carbonic anhydride through the liquid, the carbonate separates in dark brown crystals with green lustre; on boiling an aqueous solution, the same phenomena are observed as in the case of rosinduline carbonate. A further illustration is afforded by the compound, $\text{NEt} \cdot \text{C}_6\text{H}_2(\text{NH}_2) < \begin{smallmatrix} \text{N} \text{—} \\ \text{N} \end{smallmatrix} \text{Et} > \text{C}_6\text{H}_4$, obtained by the oxidation of ethylorthophenylenediamine with ferric chloride; the *hydrochloride* crystallises from water in lustrous, reddish-brown needles, and the *carbonate* is a brown, crystalline powder, readily losing

carbonic anhydride when the aqueous solution is boiled. Aniline-aposafranine yields a *carbonate* as readily as aposafranine, carbonic anhydride precipitating the salt from an ethereal solution of the base in the form of a dark red, crystalline powder.

Isorosinduline, $\text{NH}_2 \cdot \text{C}_{10}\text{H}_5 \ll \text{N}^{\text{Ph}(\text{OH})} \text{N} \gg \text{C}_6\text{H}_4$, is produced on treating the more soluble of the above-mentioned hydrochlorides isomeric with acetylrosinduline hydrochloride with boiling dilute hydrochloric acid; the hydrolysis is more advantageously effected, however, by agitating a solution of the sulphite in sulphuric acid during the careful addition of water. The *hydrochloride* crystallises from water in long, lustrous, bluish-black needles, and melts and decomposes at 270° ; the *platinochloride* is greenish-blue, and the *nitrate* crystallises in dark blue needles with bronze lustre. A comparison of the formulæ

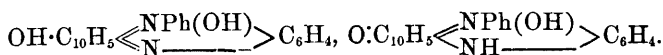


which represent rosinduline and isorosinduline respectively, explains the conversion of rosinduline bases into anhydrides, and also the fact that isorosinduline does not exhibit this property.

On boiling an aqueous solution of isorosinduline sulphate containing free sulphuric acid, the amido-group is replaced by hydroxyl, giving rise to the hydroxy-azonium base, $\text{OH} \cdot \text{C}_{10}\text{H}_5 \ll \text{N}^{\text{Ph}(\text{OH})} \text{N} \gg \text{C}_6\text{H}_4$,

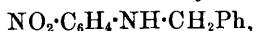
which occurs in two forms, a blue and a red modification, yielding the same salts, which are red. The blue modification may be obtained in the manner indicated, or by hydrolysing acetylisosinduline sulphite and rendering the liquid alkaline; it crystallises in lustrous, greenish-blue needles, melts and decomposes at 164° , and, although almost insoluble in cold water, yields a blue solution on boiling the liquid, which ultimately becomes turbid, owing to the production of the red modification. The *sulphate* crystallises readily, and rapidly decomposes in aqueous solution if no free acid is present; the *chloride*, $\text{OH} \cdot \text{C}_{10}\text{H}_5 \ll \text{N}^{\text{PhCl}} \text{N} \gg \text{C}_6\text{H}_4$, crystallises in dark red leaflets, and yields the red modification on treatment with soda. The *platinochloride* crystallises in dark, reddish-brown needles. The red modification of the hydroxy-azonium base is immediately formed, on warming the freshly precipitated blue modification; it crystallises from alcohol in lustrous, black prisms, and when powdered is red, melting at the same temperature as the isomeride; it is insoluble in water and in cold dilute hydrochloric and sulphuric acids. Whilst the blue modification yields a dark green solution in concentrated sulphuric acid, the isomeride develops a cherry-red coloration with the solvent, but this liquid rapidly becomes green at $50\text{--}60^\circ$. From the behaviour of the bases, it seems clear that the red salts, obtained from both forms under the influence of acids, constitute the salts of the blue modification; dilute aqueous soda, however, also dissolves the isomerides, giving rise to the sodium derivative of the red base. The latter

substance yields an *oxime*, whilst hydroxylamine has no action on the isomeride. The most reasonable explanation of the isomerism, therefore, is to be found in the following formulæ, depicting the constitution of the blue and red bases respectively.



The author now develops a system of nomenclature to meet the requirements of the following substances.

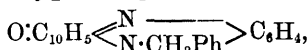
With M. TIKHVINSKY.—1 : 4-Nitrobenzylaniline,



is obtained by heating 1 : 4-chloronitrobenzene with benzylamine in a reflux apparatus for 10 hours at 180°; it crystallises from alcohol in golden-yellow prisms with blue reflex, and melts at 147°.

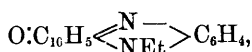
When acetamidonaphthaquinone (Abstr., 1895, i, 151) acts on benzylorthophenylenediamine, acetamidonaphthophenazine and benzylic chloride are not the only products. There is also formed *acetylbenzylrosinduline chloride*, and, on hydrolysing with dilute sulphuric acid, this is converted into *benzylrosinduline* (*benzylphenonaphthazime*).

Benzylrosindone (*benzylphenonaphthazone*),



is obtained by heating hydroxynaphthaquinone and benzylorthophenylenediamine hydrochloride with alcohol on the water bath, and treating the crystalline precipitate with boiling dilute caustic soda; it crystallises from toluene in two forms, which melt at 262—264°: short, dark red prisms with green lustre, or long, bright red needles. The solution in sulphuric acid is green.

With HERMANN FÜHNER.—*Ethylphenonaphthazone*,



is obtained by heating ethylorthophenylenediamine (1 mol.) with alcoholic hydroxynaphthaquinone for 12 hours; it crystallises from a mixture of benzene and alcohol, and melts at 192—193°. The solution in sulphuric acid is greenish-grey, and becomes orange-yellow on dilution, the *sulphate* separating in small, reddish-yellow needles.

2-Hydroxyphenylphenazone, $\text{O}\cdot\text{C}_6\text{H}_4(\text{OH}) \llcorner \begin{smallmatrix} \text{N} \text{---} \\ \text{NPh} \end{smallmatrix} \text{C}_6\text{H}_4$, is formed when a concentrated aqueous solution of phenylorthophenylenediamine hydrochloride is added to dihydroxyquinone, freshly liberated by treating the ammonium derivative with hydrochloric acid; it crystallises in reddish-brown needles, and melts at 275—280°.

2-Hydroxyethylphenazone, $\text{O}\cdot\text{C}_6\text{H}_4(\text{OH}) \llcorner \begin{smallmatrix} \text{N} \text{---} \\ \text{NEt} \end{smallmatrix} \text{C}_6\text{H}_4$, is obtained in the same way from ethylorthophenylenediamine, and crystallises from alcohol containing acetic acid in scarlet-red needles, melting at 230—240°.

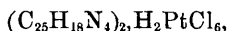
1 : 2 : 3-Methyldihydroxyphenazine, $\text{C}_6\text{HMe}(\text{OH})_2 \llcorner \begin{smallmatrix} \text{N} \\ \text{N} \end{smallmatrix} \text{C}_6\text{H}_4$, or

1 : 2-methylhydroxyphenazone, $\text{O}:\text{C}_6\text{HMe}(\text{OH})\langle\begin{smallmatrix}\text{N}^- \\ \text{NH}\end{smallmatrix}\rangle\text{C}_6\text{H}_4$, is obtained as the *hydrochloride* when a hot solution of the ammonium derivative of dihydroxytoluquinone, acidified with hydrochloric acid, is allowed to remain with orthophenylenediamine hydrochloride; the base crystallises from alcohol in brick-red needles, and melts at $265\text{--}275^\circ$. 2 : 1- or 2 : 4-Hydroxymethylphenylphenazone is obtained in the same way from phenylorthophenylenediamine; it crystallises from glacial acetic acid in dark red leaflets with coppery lustre, and melts at $245\text{--}265^\circ$. 2 : 1- or 2 : 4-Hydroxymethylethylphenazone separates from a mixture of alcohol and benzene in red crystals with blue metallic lustre, and melts at 206° . 1 : 2- or 4 : 2-Chlorhydroxymethylphenazone crystallises from alcohol in large, brownish-red prisms, and melts at $200\text{--}201^\circ$. 1 : 2- or 4 : 2-Chlorhydroxyethylphenazone crystallises in short, dark red prisms, and melts at $215\text{--}216^\circ$. 1 : 2- or 4 : 2-Chlorhydroxybenzylphenazone crystallises from glacial acetic acid in scarlet needles, and melts at 234° .

M. O. F.

Constitution of Fluorindines. By FRIEDRICH KEHRMANN and H. BÜRGIN (*Ber.*, 1896, **29**, 1246—1254; compare *Abstr.*, 1895, i, 526).—The formula for phenofluorindine suggested by Fischer and Hepp (*Abstr.*, 1890, 1444) indicates the possible existence of mono- and dialkyl, and acidyl-imide derivatives, the authors' object was to test the validity of the formula by the preparation of such compounds.

Phenylmethylphenofluorindine, $\text{C}_6\text{H}_4\langle\begin{smallmatrix}\text{NH} \\ -\text{N}\end{smallmatrix}\rangle\text{C}_6\text{HMe}\langle\begin{smallmatrix}\text{N}^- \\ \text{NPh}\end{smallmatrix}\rangle\text{C}_6\text{H}_4$, has been previously described (*loc. cit.*); the *platinochloride*,



is an indigo crystalline powder. When boiled with ethylic benzoate, the base yields the *benzoyl* derivative; this crystallises in dark red prisms of golden lustre, is insoluble in alcohol, and is readily hydrolysed by alcoholic sulphuric acid (50 per cent.); this method of preparing benzoyl derivatives is applicable to all monalkyl-fluorindines. The *hydrochloride* is readily soluble in alcohol, the solution is blue but not fluorescent, it crystallises in small, violet needles of coppery lustre, and readily regenerates the benzoyl derivative when heated at 110° , or by the action of ammonia on the alcoholic solution.

Phenylphenofluorindine, $\text{C}_6\text{H}_4\langle\begin{smallmatrix}\text{NH} \\ -\text{N}\end{smallmatrix}\rangle\text{C}_6\text{H}_2\langle\begin{smallmatrix}\text{N}^- \\ \text{NPh}\end{smallmatrix}\rangle\text{C}_6\text{H}_4$, is prepared by the interaction of 2-hydroxyphenylphenazone, or the hydrochloride of the oxidation product of orthamidodiphenylamine, with orthophenylenediamine hydrochloride; it is identical with Fischer and Hepp's compound from aposafranine and orthophenylenediamine (this vol., i, 323) their statement (*Abstr.*, 1895, i, 220) that diphenylphenofluorindine is formed from orthophenylenediamine and the oxidation product of orthamidodiphenylamine is, therefore, incorrect. The hydrochloride crystallises in canthradine green needles, and its alcoholic or sulphuric acid solution has a brownish-red

fluorescence with a tinge of violet. The *benzoyl* derivative is obtained as a granular powder, and is less soluble than the base; the *hydrochloride* gives a blue nonfluorescent solution with alcohol, and in other respects resembles the corresponding compound described above. Fischer and Hepp describe the base as crystallising unchanged from ethylic benzoate.

Diphenylphenofluorindine, $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{NPh} \\ \diagup \quad \diagdown \\ \text{---} \text{N} \end{smallmatrix} \text{C}_6\text{H}_2 \begin{smallmatrix} \text{N} \text{---} \\ \diagdown \quad \diagup \\ \text{NPh} \end{smallmatrix} \text{C}_6\text{H}_4$, prepared by the condensation of orthamidodiphenylamine with its oxidation product, is identical with the compound obtained by Fischer and Hepp from azophenine and mercuric oxide (Abstr., 1895, i, 220); the dihydrochloride is deposited in crystals of coppery lustre and differs from that of the monophenylfluorindine by its greater solubility in alcohol; the solution is blue with a violet-brown fluorescence; the addition of ammonia changes the colour to violet-red with a yellowish brick-red fluorescence which quickly disappears as the base is deposited.

Methylphenofluorindine, $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{NMe} \\ \diagup \quad \diagdown \\ \text{---} \text{N} \end{smallmatrix} \text{C}_6\text{H}_2 \begin{smallmatrix} \text{N} \text{---} \\ \diagdown \quad \diagup \\ \text{NH} \end{smallmatrix} \text{C}_6\text{H}_4$, is prepared by heating at 260° the hydrochloride of the oxidation product of methylorthophenylenediamine with orthophenylenediamine hydrochloride and benzoic acid; it is probably identical with the compound prepared by Fischer and Hepp from orthodiamidophenazine and methylorthophenylenediamine; the base is a dark red, somewhat unstable, powder, the aqueous and alcoholic solutions of which are violet-red with a garnet-red fluorescence; the *dihydrochloride* crystallises in microscopic plates having a bronze lustre. J. B. T.

Tropinic acid. By GIACOMO L. CIAMICIAN and PAUL SILBER (*Ber.*, 1896, 29, 1216—1218).—When tropinic acid is heated at 220° for 8 hours with hydriodic acid and phosphorus, it yields a base, the aurochloride of which forms yellow crystals melting at $208\text{--}210^\circ$. Although the composition of this salt is identical with that of piperidine aurochloride, and the melting point does not differ much from that of the latter, yet the crystals do not appear to be identical. The compound is being further examined. A. H.

Quinine as a Developer. By EDWIN ACKERMANN (*Bull. Soc. Chim.*, 1895, [3], 13, 915—917).—On heating in a closed tube at 100° for 10 hours a mixture of 2 grams of quinine sulphate, 8 grams of zinc dust, and 40 c.c. of water, a liquid having strong reducing properties is obtained. This serves as an excellent developer, producing a clear and sharp image. J. F. T.

Microscopic Discrimination of Cinchonidine and Homocinchonidine. By TH. H. BEHRENS (*Zeit. anal. Chem.*, 1896, 35, 133—143).—Hesse, whilst maintaining the individuality of homocinchonidine against Skraup, Claus, and de Vrij, who regard it as impure cinchonidine, has published methods for the conversion of the one into the other (Abstr., 1890, 1166). The author endeavours

by microscopic methods to solve the question whether cinchonidine can, by the addition of other cinchona alkaloids, be caused to assume the properties of homocinchonidine or the converse.

A 0.5 per cent. solution of the mixed hydrochlorides fractionally precipitated with sodium hydrogen carbonate deposits, first the cinchonidine in groups of filiform needles with a marked tendency to ramify at the ends (difference from cinchonine crystals, which do not ramify). Homocinchonidine yields broad, six-sided plates, and large stellate groups with broad foliated rays. Another method consists in subliming the bases and warming the sublimates with water until crusts begin to form. The same difference is observed as in the sodium carbonate precipitate. Still more distinct are the forms of the platinochlorides:—Cinchonidine yields minute spheroids which are at first clear and structureless, but gradually become turbid with radial fibrous crystals which rarely extend beyond the edge of the spheroid. Homocinchonidine yields large radiating dendrites and rosettes. A similar and highly characteristic difference is observed between the acid hydriodides.

The general tendency of homocinchonidine salts seems to be to form larger crystals than those of cinchonidine. Addition of quinine to a small crystallising cinchonidine salt does not cause it to furnish the large crystals of homocinchonidine. Fractional sublimation of mixtures of quinine, quinidine, and cinchonidine never yielded the characteristic crystals of homocinchonidine. Mixtures of quinine, quinidine, and homocinchonidine fractionally precipitated by sodium hydrogen carbonate never yielded the radiating, thread-like crystals of cinchonidine. Hesse's methods for the conversion of one alkaloid into the other were repeated, but the characteristic crystalline forms of each substance were not affected. A great variety of specimens of commercial cinchonidine, homocinchonidine, and "quinetum" were examined by the fractionation methods and by precipitation with platinic chloride, and in all of them a proportion, frequently a preponderance, of the large, crystallising substance was found.

A plate of drawings of the microscopic crystals accompanies the paper. M. J. S.

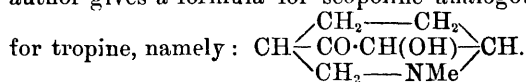
Scopolamine. By WALTER LUBOLDT (*Chem. Centr.*, 1895, ii, 896—897; compare Schmidt, *Abstr.*, 1895, i, 158).—Crystallised scopolamine, $C_{17}H_{21}NO_4 + H_2O$, is best obtained from the hydrobromide; an aqueous solution of the latter, rendered alkaline with potassium carbonate, is extracted with chloroform, the solution evaporated, the residue extracted with ether, and the ethereal solution treated with the calculated quantity of water. It melts at 56° , and has a specific rotary power $[\alpha]_D = -14^\circ 58'$ in aqueous and still lower in alcoholic solution.

When left in contact with concentrated sulphuric acid for a short time, water is withdrawn, but, on further contact, scopoline and atropic acid are produced. The author has obtained the compounds $C_{34}H_{40}N_2O_7 \cdot (HAuCl_4)_2$ and $(C_{17}H_{19}NO_3)_2 \cdot H_2PtCl_6$.

Scopoline, obtained from scopolamine by hydrolysing with baryta water, melts at 109° ; the *hydrochloride*, *hydriodide*, *sulphate*, and

mandelate (m. p. 112°) have been analysed. Concentrated hydriodic acid at 150 – 160° , concentrated sulphuric and acetic acids are without action on scopoline. On oxidation with potassium permanganate, the base yields a new compound, *scopoligenine*, which melts at 205 – 206° ; its *aurochloride* melts at 235 – 236° ; its *platinochloride* forms brown-red crystals; its *nitroso*-derivative melts at 174 – 175° , and, when treated with methylic iodide, is converted again into a scopoline salt.

Scopoline, when treated with methylic iodide, yields Hesse's scopolinemethylammonium iodide; the corresponding *chloride*, *aurochloride* (m. p. 246°), and *platinochloride* (m. p. 238°) are described. Scopolaminemethylammonium iodide, on treatment with silver oxide, yields *methyloscopoline*, which boils at 244° , and with methylic iodide forms *methyloscopolinemethylammonium iodide*, the *chloride* of which melts at 250° , the *aurochloride* at 191° , and the *platinochloride* at 243 – 244° . On treatment with potash, it is decomposed into a ketone, $C_7H_5O_2$, trimethylamine, water, and potassium iodide. The author gives a formula for scopoline analogous to Merling's formula



J. J. S.

Albumoses. By HUGO SCHRÖTTER (*Monatsh.*, 1896, **17**, 199–205; compare Henninger, *Abstr.*, 1878, 802, 989).—The author has treated the albumoses previously obtained by him (*Abstr.*, 1894, i, 215), their hydrochlorides, and also Paal's peptone hydrochloride with acetic anhydride, according to Henninger's method, and finds that the albumoses, but not the true peptones, yield products which are to be regarded not as regenerated albumin, as Henninger states, but as simple acetyl derivatives of albumoses. Henninger's assumption that peptones are formed by the addition of water to albumin is, therefore, no longer tenable.

J. J. S.

Saline Compounds of Casein and their Uses. By FRANZ RÖHMANN (*Chem. Centr.*, 1895, ii, 684–685; from *Berl. Klin. Woch.*, **32**, 519–522).—Casein is a substance with acid properties, and dissolves in alkalis to form both acid and neutral salts. The alkali salts exhibit only a slight fluorescence; the acid calcium salt forms a milk-white solution; cow's milk probably owes its colour, to some extent, to the presence of this salt. Concentrated solutions of the sodium salt are readily precipitated by acetone, the calcium salt by alcohol; after washing with absolute alcohol and then with ether, the salts were obtained as white powders.

According to the author, the acid sodium salts (that is those acid to phenolphthalein) appear to be the most useful for diabetic purposes. With the aid of these salts, the author has obtained mixtures corresponding with cows' and human milk.

Casein silver is best precipitated by alcohol, and forms a white powder, which is readily soluble in warm water, giving a slightly opalescent solution

J. J. S.

Reaction of Bilirubin with Iodine and Chloroform. By JOHN L. W. THUDICHUM (*J. pr. Chem.*, 1896, [2], 53, 314—324).—Half a gram of bilirubin was dissolved in rather more than a litre of chloroform, and an excess of a solution of iodine in absolute alcohol was added; the liquid became deep red, and if exposed to the light or warmed, a green substance separated, but this was not biliverdin. By shaking the chloroform solution with caustic soda and acidifying the extract, two violet compounds were isolated; the extracted chloroform solution was at first colourless, but speedily became rose coloured and then yielded a rose coloured substance by treatment with caustic soda. On distillation, the chloroform solution gave a volatile acid yellow compound.

The foregoing experiment was made in view of Jolles's statement that bilirubin can be quantitatively oxidised to biliverdin by iodine in alcoholic solution. Jolles bases a long paper on this false premise (*Abstr.*, 1894, ii, 466) and in consequence nearly all the conclusions contained therein are erroneous, as the author shows at some length.

A. G. B.

Hæmatin. By WILLIAM KÜSTER (*Ber.*, 1896, 29, 821—824).—The author uses the term "hæmin" for the complex $C_{32}H_{31}ClN_4FeO_3$, and "hæmatin" for the substance derived from this by the action of alkalis, in which the chlorine has been replaced by OH. He has prepared a hæmatin acetate of the composition



He has also obtained two specimens of hæmin with the composition $C_{32}H_{33}ClN_4FeO_3$ (one of them crystallised with $\frac{1}{6}$ mol. of amyl alcohol), and one specimen with CH_2 more than this, whilst a hæmatin bromide which he prepared had the composition $C_{31}H_{31}BrN_4FeO_3 \cdot EtOH$; the hæmin prepared by Cloëtta's method contains, as Cloëtta himself states, only 3 atoms of nitrogen.

By oxidising hæmatin, two new acids were obtained; namely, *dibasic hæmatic acid*, $C_8H_{10}O_5$, which melts at 112—113°, and yields, on further oxidation, the *anhydride of tribasic hæmatic acid*; this anhydride, $C_8H_8O_5$, melts at 94—95°. A third substance, which contains iron and is soluble in sodium carbonate, was also obtained.

C. F. B.

A Phosphorised Constituent of Plant-seeds. By ERNST SCHULZE and ERNST WINTERSTEIN (*Zeit. physiol. Chem.*, 1896, 22, 90—94).—By extracting powdered seeds with a 10 per cent. solution of sodium chloride, a substance is precipitated with the proteid at 80°, which goes into solution on cooling. It is free from nitrogen, but contains phosphorus (Palladin, *Abstr.*, 1894, i, 631). Analysis gave the following result: C, 9.65; H, 2.83; and ash 67.88 per cent. Of the ash, more than half consists of phosphoric anhydride. The nature of the material is still uncertain.

W. D. H.

Organic Chemistry.

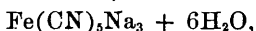
Peculiar Decomposition of Diiodoacetylene. By VICTOR MEYER and WILHELM PEMSEL (*Ber.*, 1896, **29**, 1411—1412).—Baeyer has shown (*Abstr.*, 1885, 1199) that when diiodoacetylene is subjected to the action of light or heat, it is changed into a new substance melting at 184°. This is not, as he supposed, hexaiodobenzene, but tetraiodoethylene, C_2I_4 ; it crystallises in large prisms and melts, when pure, at 187° without decomposing, hence the specimen obtained by Homolka and Stoltz must have been impure, as it melted and decomposed about 165°.

The tetraiodoethylene is accompanied by a black, totally insoluble powder, containing a large proportion of carbon together with small quantities of iodine, hydrogen, and oxygen. A. L.

Supposed Compound of Cyanoform and Mercuric Iodide. By ANTONIO LONGI and G. MAZZOLINO (*Gazzetta*, 1896, **26**, i, 274—280). Pfankuch (this Journal, 1871, 901; 1873, 362) obtained a compound to which he assigned the composition $2CH(CN)_3, 3HgI_2$, by heating mercuric cyanide, iodoform, and alcohol in a closed tube; Claus (*ibid.*, 1876, ii, 934), however, was unable to prepare this substance. By heating the three substances together at 150—160° for two days, hydrogen cyanide, carbonic oxide and anhydride, methane, an oil having the odour of an isonitrile, formic acid, and metallic mercury are obtained; from the product, the crystalline substance described by Pfankuch can be separated, but it consists of Boullay's double iodide having the composition HgI_2, NH_4I, H_2O . The double compound of cyanoform and mercuric iodide seems therefore not to exist.

W. J. P.

Sodium Nitroferrocyanides. By KARL A. HOFMANN (*Zeit. anorg. Chem.*, 1896, **12**, 146—168). *Trisodiumferrocyanide*,



the mother substance of the series of compounds already described by the author (this vol., i, 197, 269), is obtained by adding phenylhydrazine (10 parts) to a mixture of sodium nitroferrocyanide (10 parts) and water (20 parts) cooled to -3°, when nitrogen is evolved. The mixture is allowed to remain two hours in the freezing bath, and then diluted with three times the volume of alcohol; this dissolves a red organic colouring matter which is formed and any unaltered sodium nitroferrocyanide, whilst a resinous, red substance remains behind. The latter is dissolved in air-cold water, mixed with a 10 per cent. solution of sodium hydroxide (20 c.c.), and precipitated with alcohol; the filtrate is mixed with more alcohol, and crystallised by prolonged cooling at 0°. The first precipitate is often contaminated with a small quantity of sodium ferrocyanide, the second precipitate is usually pure. It crystallises in reddish-yellow aggregates consisting of slender needles, gives an intense reddish-yellow

solution with water, which, on addition of dilute acids, turns bright green. With ammonium sulphide it gives no coloration. When heated with hydroxylamine hydrochloride and sodium hydroxide, it gives a beautiful red coloration. When heated with sodium hydroxide, it is decomposed with formation of ferric hydroxide and sodium ferrocyanide, but no ammonia is evolved. With ferrous sulphate, it gives a bluish-white precipitate; with ferric chloride, a dark blue, and with sodium nitrite and acetic acid, a beautiful violet solution. When treated with a neutral solution of iodine, it is converted into a ferricyanide derivative, whereby 1 atom of iodine is used up for each atom of iron.

Trisodium ferrocyanide is very easily converted into sodium nitroferrocyanide by treating the aqueous solution with nitric oxide, or by mixing it with sodium nitrite. Since in the latter case no evolution of gas or heat takes place, the reaction must be considered as the formation of a double salt, and therefore the quaternary sodium nitroferrocyanide is expressed by the formula $\text{Fe}(\text{CN})_5\text{Na}_3\text{NaNO}_2$. Since secondary sodium nitroferrocyanide yields the quaternary salt when treated with sodium hydroxide, without oxidation or reduction taking place, it can be expressed by the formula $\text{Fe}(\text{CN})_5\text{NONa}_2$. The compounds of nitroferrocyanic acid with alcohols, which have been already described are also double salts of the formula



Sodium arseniteferrocyanide, $\text{Fe}(\text{CN})_5\text{AsO}_3\text{Na}_4\text{H}_2 + 9\text{H}_2\text{O}$ or $\text{Fe}(\text{CN})_5\text{AsO}_2\text{Na}_4 + 10\text{H}_2\text{O}$, is obtained by adding a solution of sodium arsenite to a solution of sodium nitroferrocyanide containing sufficient sodium hydroxide for the formation of the quaternary salt. The solution is concentrated over sulphuric acid in a vacuum, the sodium arsenate which separates out being removed from time to time. It crystallises in microscopic, thin, yellow needles. The yellow aqueous solution gives no coloration with ammonium sulphide, and no ammonia with sodium hydroxide; with ferrous sulphate, a white precipitate, which turns bright blue on addition of hydrochloric acid; with ferric chloride, a beautiful violet solution, and when boiled with hydroxylamine hydrochloride and sodium hydroxide, an intense bluish-red solution. The *potassium* salt with $4\text{H}_2\text{O}$ crystallises in yellow aggregates, consisting of radiating needles. Both salts decolorise iodine and permanganate solutions. These compounds are analogous to the sulphite compound already described. Both are stable towards alkali cyanides at the ordinary temperatures, and when heated with alkali cyanide yield alkali ferrocyanide. The arsenite compound, when treated with sodium sulphite at the ordinary temperature, is converted into the sulphite compound. The author was unable to obtain analogous compounds with sodium antimonite, phosphite, or hypophosphite.

The sodium amidoferrocyanide, $\text{Fe}(\text{CN})_5\text{Na}_3\text{NH}_2\cdot 6\text{H}_2\text{O}$, previously described by the author (this vol., i, 69), is an ammonium salt of the formula $\text{Fe}(\text{CN})_5\text{Na}_3\text{NH}_3\cdot 6\text{H}_2\text{O}$, since it is easily obtained by the action of strong ammonia on trisodium ferrocyanide, and that without any evolution of gas. This ammonia compound is converted, with-

out oxidation or reduction taking place, when treated with sodium nitrite, sodium sulphite, or sodium cyanide, into quaternary sodium nitroferrocyanide, sodium sulphite ferrocyanide, or sodium ferrocyanide respectively.

All the sodium nitroferrocyanides which contain the group $\text{Fe}(\text{CN})_5$, yield a red colouring matter, when heated with hydroxylamine and sodium hydroxide. This is precipitated by alcohol as a red powder. It is soluble in water, not altered by zinc dust and sodium hydroxide, and decolorised by permanganate or dichromate solution, but the colour is again produced when heated with hydroxylamine and sodium hydroxide. When exposed to the air, it turns yellow, and is converted into the above ammonium compound



The violet coloration produced by treating alkali sulphides with nitroferrocyanides is probably due to the formation of a reduction product, but the author was unable to isolate this in a satisfactory manner.

Sodium nitroferrocyanide, when treated with potassium cyanide, gives a beautiful, bluish-red coloration, and the solution shows a broad absorption band between the D and F lines, but all attempts to isolate the compound resulted in the formation of potassium ferrocyanide.

E. C. R.

Chloraloses. By MAURICE HANRIOT (*Compt. rend.*, 1896, **122**, 1127—1129; compare *Abstr.*, 1895, i, 321).—Galactose combines readily with chloral at 100° in presence of a small quantity of hydrochloric acid, and yields a mixture of α - and β -galactochloral, $\text{C}_8\text{H}_{11}\text{Cl}_3\text{O}_6$. The latter crystallises from water or methylic alcohol in nacreous lamellæ which melt at 202° , and do not sublime readily even under reduced pressure, and are almost insoluble in water or ether. It has no action on Fehling's solution, and gives a red coloration with a hydrochloric acid solution of orcinol. The *tetracetyl* derivative melts at 125° , and is insoluble in water or ether, but very soluble in alcohol and chloroform. The *tribenzoyl* derivative forms long needles, which melt at 141° , and dissolve in benzene and in methylic and ethylic alcohols.

When oxidised with permanganate, the galactochloral yields a chloralic acid, $\text{C}_7\text{H}_7\text{Cl}_3\text{O}_6$, which melts at 307° , and is identical with the acid obtained from arabinochloral.

Levulose, under similar conditions at 80° , yields *levulochloral*, $\text{C}_8\text{H}_{11}\text{Cl}_3\text{O}_6$, which crystallises in long needles melting at 228° , and is very soluble in hot water or alcohol. Its benzoyl derivative is amorphous.

C. H. B.

Separation of Methylamines. By MARCEL DELÉPINE (*Compt. rend.*, 1896, **122**, 1064—1066).—The method is based on the observation of Henry that with formaldehyde, methylamine yields the compound $(\text{CH}_2\cdot\text{NMe})_3$ boiling at 166° , dimethylamine the compounds $\text{OH}\cdot\text{CH}_2\cdot\text{NMe}_2$ and $\text{CH}_2(\text{NMe}_2)_2$ boiling at 80 — 85° , whilst trimethylamine, the author assumes, remains unaltered, and continues to boil at 9° . The quaternary salt and any ammonium salts

are removed by the known methods, and the vapour of the mixture of amines is passed into a well cooled 40 per cent. solution of formaldehyde. The product is then poured over an equal weight of potassium hydroxide, contained in a flask attached to a condenser the open end of which dips into a suitable solvent. The greater part of the trimethylamine volatilises and the residual liquid separates into two layers, the upper of which contains the mono- and di-methylamine derivatives. In consequence of the considerable differences in the boiling points, separation by fractionation presents no difficulties, and the amines are readily regenerated by the action of a boiling mixture of hydrochloric acid and alcohol.

C. H. B.

Oxime of Glucosamine Hydrochloride. By ERNST WINTERSTEIN (*Ber.*, 1896, **29**, 1392—1393).—Glucosamine hydrochloride reacts with hydroxylamine to form the *oxime*, which crystallises in small masses of radiating, lustrous needles, and melts at 166°. The author proposes to study the configuration of this compound.

A. H.

Hydroxylamine Fumarate and its Products of Decomposition. By SIMEON M. TANATAR (*Ber.*, 1896, **29**, 1477—1479).—*Hydroxylamine fumarate* is obtained in monoclinic needles by mixing cold concentrated aqueous solutions of hydroxylamine hydrochloride and potassium fumarate in equivalent quantities; when warmed in aqueous solution on the water bath, it loses carbonic anhydride, the ammonium salts of inactive aspartic and other acids being formed at the same time.

C. F. B.

α -Halogen Ketoximes. By ROLAND SCHOLL and GEORG MATTHAIPOULOS (*Ber.*, 1896, **29**, 1550—1558).—*Chloracetoxime*,



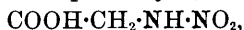
is obtained by treating chloracetone, prepared by Fritsch's method (*Abstr.*, 1893, i, 303, and 1894, i, 490), with rather less than the theoretical amount of hydroxylamine hydrochloride and sodium carbonate. A little methylglyoxime, $\text{NOH}\cdot\text{CH}\cdot\text{CMe}:\text{NOH}$, is always formed at the same time, and it is the only product if about three times the above quantity of hydroxylamine is used. Chloracetoxime boils at 71.2°, 84.5°, 98.0°, and 171° under 9, 21, 45, and 727 mm. pressure respectively, decomposing slightly at the last temperature. When its ethereal solution was treated with liquid nitric peroxide, a few crystals, melting at 167—168°, were obtained, but the main product was an unstable oil, doubtless *chloropropylpseudonitrole*, $\text{CH}_2\text{Cl}\cdot\text{CMe}(\text{NO}_2)\cdot\text{NO}$, which, when oxidised with chromic acid in acetic acid solution, yielded a small quantity of *chlorodinitropropane*, $\text{CH}_2\text{Cl}\cdot\text{CMe}(\text{NO}_2)_2$, boiling at 103—105° under 15.4 mm., and, with slight decomposition, at 200—202° (uncorr.) under atmospheric pressure. Attempts to convert the chloropseudonitrole into chloropropylene have been as yet unsuccessful.

Bromacetoxime, prepared in a similar manner, melts at 36.5°, and boils, without decomposition if small quantities are used, at 82.8° under 8 mm. pressure. It was less easy to obtain pure products from

it than was the case with the chloro-compound. Bromacetone could probably be best obtained pure by the method described below in the case of iodacetone.

Iodacetone has been obtained pure for the first time by treating pure chloracetone with a concentrated aqueous solution of potassium iodide, and then adding methylic alcohol; it is a faintly yellowish liquid boiling at 58.4° under 11 mm. pressure. The *oxime* melts at 64.5° ; when it is treated with nitric peroxide there is no sign of the formation of a pseudonitrile. C. F. B.

Nitramineacetic acid. By ARTHUR R. HANTZSCH and W. V. METCALF (*Ber.*, 1896, **29**, 1680—1685).—*Ethylic urethaneacetate*, $\text{COOEt}\cdot\text{CH}_2\cdot\text{NH}\cdot\text{COOEt}$, prepared by Curtius' method from ethylic chlorocarbonate and ethylic amidoacetate, crystallises in long, colourless prisms, melting at $24.5\text{--}27^{\circ}$, and boiling at $145\text{--}146^{\circ}$ (22 mm.); it is hygroscopic, and is only deposited in crystals if the solvent is anhydrous. The yield is 75—80 per cent. of the theoretical. *Urethaneacetic acid*, $\text{COOH}\cdot\text{CH}_2\cdot\text{NH}\cdot\text{COOEt}$, prepared by the action of concentrated hydrochloric acid on the preceding compound, is crystalline, stable towards acids, decomposes carbonates, and melts at $67\text{--}69^{\circ}$. *Ethylic nitrosourethaneacetate*, $\text{COOEt}\cdot\text{CH}_2\cdot\text{N}(\text{NO})\cdot\text{COOEt}$, obtained from the ethylic salt and nitrous anhydride, is a yellow, odourless oil, stable when pure, and volatile with steam; it is resolved into its constituents by the action of hydrochloric acid. *Ethylic nitrourethaneacetate* is formed by the action of concentrated nitric acid on the ethylic salt; it is a yellow oil, and with dry ammonia yields *ethylic nitramineacetate*, $\text{COOEt}\cdot\text{CH}_2\cdot\text{N}_2\text{O}_2\text{H}$, which is crystalline, and melts at $24\text{--}25^{\circ}$; it decomposes carbonates, and is somewhat hygroscopic, but only dissolves slowly in water. The yield is about 90 per cent. of the theoretical. The salts are readily soluble; the *copper* salt forms well developed crystals; the *ammonium* salt melts and decomposes at about 60° . *Nitramineacetic acid* is obtained by the hydrolysis of the ethylic salt at low temperatures by means of either alkali or acid; it is dibasic, crystallises in long needles, and melts and decomposes at $103\text{--}104^{\circ}$. The *mercurous* and *lead* salts are sparingly soluble; the *potassium* and *silver* salts are crystalline and explosive, the latter darkens on exposure to light, and gives a mirror when boiled with water; the *copper* salt is deposited in blue crystals containing $2\text{H}_2\text{O}$. The salts and acid give a red coloration with ferric chloride, and the acid itself at 125° yields carbonic anhydride, nitrous oxide, and methylic alcohol, together with a substance which volatilises with difficulty, and is being further investigated; this indicates that the acid is probably not a true nitramine,



but a hydroxyl compound such as $\text{COOH}\cdot\text{CH}_2\cdot\underset{\text{OH}\cdot\text{N}}{\underset{|}{\text{N}}}>\text{O}$, but acetic chloride, acetic anhydride, and phosphoric anhydride do not react with the acid at medium temperatures; when distilled with soda or baryta, carbonic anhydride and nitrogen are produced.

J. B. T.

Composition of Wool-fat. III. By L. DARMSTAEDTER and ISAAC LIFSCHÜTZ (*Ber.*, 1896, **29**, 1474—1477).—The residual wool-fat, left after the treatment described in the preceding communications (this vol., i, 198, 346), was treated with fusel oil, and the wool-wax so obtained was hydrolysed with alcoholic potash. From the product, the alcohols were separated by extraction with light petroleum; they amounted to 26—30 per cent. of the wax, and consisted of cetylic alcohol, melting at 76—77°, another alcohol melting at 66—68°, and cholesterol. The soaps were partly soluble in alcohol, partly insoluble. The insoluble part amounted to 33—36 per cent. of the wax. When cautiously treated with dilute hydrochloric acid, it yields *lanoceric acid*, $C_{30}H_{60}O_4$, apparently a dihydroxy-acid. This acid softens at 102°, and melts at 104—105°; it then solidifies again at 101—103°, and now melts again at the same temperature as before. It has, however, lost a molecule of water, probably from between the two hydroxyl groups, for it still has acid properties. The acid very readily forms a lactone, for example, when boiled with dilute hydrochloric acid, the lactone melts at 86°. When the acid is boiled with alcohol and strong hydrochloric acid, it is converted into a neutral substance, melting at 95—97°.

C. F. B.

Conversion of Tariric and Stearolic acids into Stearic acid. By A. ARNAUD (*Compt. rend.*, 1896, **122**, 1000).—Tariric and stearolic acids, $C_{18}H_{32}O_2$, are isomeric acids of the $C_nH_{2n-4}O_2$ series, but all attempts to convert them into stearic acid by hydrogenation have hitherto failed. If, however, one part of either acid is heated in sealed tubes at 200—210° with 10 parts of concentrated hydriodic acid and a small quantity of amorphous phosphorus, it yields a mixture of solid acids of the acetic series, from which stearic acid can be separated in considerable quantity by crystallisation from strong alcohol.

C. H. B.

Spectrochemical Investigation of the Ethereal Salts of α - and β -Mesityloxidoxalic acid. By JULIUS W. BRÜHL (*Annalen*, 1896, **291**, 137—146).—According to the accepted view of their constitution, the ethereal salts of α -mesityloxidoxalic acid (Claisen, this vol., i, 561) should exhibit a higher molecular refraction and dispersion than the corresponding derivatives of the β -acid. The author's investigation shows that this is actually the case, and illustrates the influence of the solvent on the labile compounds under discussion.

M. O. F.

Tetronic acid. By LUDWIG WOLFF [and CARL SCHWABE] (*Annalen*, 1896, **291**, 226—252; compare this vol., i, 87, and 277).—It having been shown (*loc. cit.*) that tetric acid is a γ -lactone, it became desirable to prepare and investigate tetronic acid, $\begin{matrix} \text{CO}\cdot\text{CH}_2 \\ | \\ \text{CH}_2\cdot\text{CO} \end{matrix} > \text{O}$, the lactone of which tetric acid is a methyl derivative.

Bromotetronic acid, $\begin{matrix} \text{CO}-\text{CH}_2 \\ | \\ \text{CHBr}\cdot\text{CO} \end{matrix} > \text{O}$, is obtained by heating ethylic di-

bromacetoacetate under a pressure of 30—40 mm. during 2—3 hours at 120—130°; it crystallises from water in white needles or prisms, becomes yellow at 160°, and melts and decomposes at 183°. An aqueous solution develops a dark red coloration with ferric chloride, and a violet coloration with sodium nitrite; it reduces Fehling's solution and potassium permanganate, and liberates carbonic anhydride from carbonates. The *calcium* and *barium* salts dissolve readily in water, and crystallise in white needles or prisms; the *silver* salt crystallises from water in slender needles.

Tetronic acid, $\begin{array}{c} \text{CO}\cdot\text{CH}_2 \\ | \\ \text{CH}_2\cdot\text{CO} \end{array} > \text{O}$, is prepared by reducing bromotetronic acid with sodium amalgam in an atmosphere of carbonic anhydride, and crystallises from a mixture of alcohol and petroleum in lustrous plates, and from warm water in prisms; it sinters at 135°, and melts at 141°. Its behaviour towards ferric chloride, sodium nitrite, Fehling's solution, and potassium permanganate is the same as that of the bromo-derivative. The *calcium* salt contains $2\frac{1}{2}\text{H}_2\text{O}$, but can be crystallised in needles, which contain $4\text{H}_2\text{O}$, and lose $1\frac{1}{2}$ mol. on exposure to air; the *copper* salt crystallises in green needles, and the *silver* salt dissolves readily in water. When the reduction of bromotetronic acid is carried out in the ordinary manner, and carbonic anhydride is not led into the liquid, an *acid* of the formula $\text{C}_{10}\text{H}_{10}\text{O}_6$ is produced; it crystallises from hot water in vitreous needles or prisms, melts and evolves gas at 209°, and develops no coloration with ferric chloride or sodium nitrite. The *phenylhydrazide* or *hydrazone* of tetronic acid, $\begin{array}{c} \text{NHPh}\cdot\text{NH}\cdot\text{C}-\text{CH}_2 \\ | \\ \text{CH}\cdot\text{CO} \end{array} > \text{O}$, or $\begin{array}{c} \text{NHPh}\cdot\text{N}:\text{C}-\text{CH}_2 \\ | \\ \text{CH}_2\cdot\text{CO} \end{array} > \text{O}$, crystallises from dilute alcohol in white prisms, and melts at 128°; the solution in concentrated sulphuric acid is bluish-violet, and becomes red on adding potassium dichromate. *Benzoyltetronic acid*, $\begin{array}{c} \text{OBz}\cdot\text{C}\cdot\text{CH}_2 \\ | \\ \text{CH}\cdot\text{CO} \end{array} > \text{O}$, is obtained by agitating aqueous tetronic acid with benzoic chloride and sodium carbonate; it crystallises from a mixture of chloroform and petroleum in lustrous leaflets or prisms, and melts at 120°.

Dibromotetronic acid, $\begin{array}{c} \text{CO}\cdot\text{CH}_2 \\ | \\ \text{CBr}_2\cdot\text{CO} \end{array} > \text{O}$, is obtained by treating a solution of tetronic acid in chloroform with bromine in presence of water, bromotetronic acid being produced when this agent is absent. The acid, however, is unstable, and undergoes spontaneous conversion into a mixture of tribromomethylketole, bromotetronic acid, and, possibly, dibromomethylketole. Alkali carbonates decompose dibromotetronic acid, giving rise to bromoform.

Tribromomethylketole, $\text{CBr}_3\cdot\text{CO}\cdot\text{CH}_2\cdot\text{OH}$, is obtained by adding bromine to bromotetronic acid suspended in water, and heating the liquid on the water bath until carbonic anhydride ceases to be evolved; it crystallises from acetone or methylic alcohol in lustrous, rhombic leaflets, which sinter at 168°, and melt, evolving gas, at 174°. Fehling's solution and potassium permanganate are reduced when gently heated, and hot sodium carbonate resolves the substance into bromoform and glycollic acid; bromoform obtained in

this way melts at 9° , and boils at 146° . When concentrated ammonia acts on dibromotetronic acid, dibromacetamide is produced.

α -Dibromomethylketole, $\text{CBr}_2\text{Me}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{OH}$, is produced when bromine is added to methyltetronic acid suspended in water, and the liquid heated on the water bath until the evolution of carbonic anhydride ceases; it crystallises from a mixture of chloroform and petroleum in lustrous leaflets, and melts at 85° . It quickly reduces Fehling's solution and an ammoniacal solution of silver.

Oximidoetronic acid, $\text{NOH}\cdot\overset{\text{CO}\cdot\text{CH}_2}{\underset{\text{CO}}{\text{C}}}>\text{O}$, is obtained by acidifying with hydrochloric acid a solution of sodium nitrite in which tetronic acid has been suspended during 15 minutes; it crystallises from water in yellow leaflets, and melts at 136° evolving gas, or when rapidly heated, at 144° . It is strongly acidic, and the alkali salts are deep violet, and the silver salt separates in crystals having a greenish lustre. The acid is an unstable substance, and becomes brown when exposed to light; boiling water eliminates hydrogen cyanide. Whilst nitrous acid converts methyltetronic acid into α -oximidopropionylglycollic acid (this vol., i, 88), bromotetronic acid yields oximidotetronic acid; dibromotetronic acid is also produced, arising from the action of hypobromous acid on bromotetronic acid.

Dioximidobutyrolactone, $\text{NOH}\cdot\overset{\text{NOH}\cdot\text{C}\cdot\text{CH}_2}{\underset{\text{NOH}\cdot\text{C}-\text{CO}}{\text{C}}}>\text{O}$, slowly separates from a solution of oximidotetronic acid in hydrochloric acid, and crystallises from water in lustrous prisms containing $1\text{H}_2\text{O}$; the water is removed at 100° , and the anhydrous substance becomes brown and melts, evolving gas, at 178° . The dioxime is acidic in character, and forms several crystalline metallic derivatives.

Oximidobromomethylbutyrolactone, $\overset{\text{C}(\text{NOH})\cdot\text{CH}_2}{\underset{\text{CMeBr}-\text{CO}}{\text{C}}}>\text{O}$, is obtained by the action of hydroxylamine on finely powdered bromomethyltetronic acid suspended in water; it crystallises from a mixture of ether and petroleum in large, transparent prisms, and melts at 128° . The substance is feebly acidic, and dissolves slowly in soda and ammonia; it is decomposed by water at 80 — 90° , yielding diacetyl, carbonic anhydride, and brominated products.

Anhydrotetronic acid, $\text{C}_5\text{H}_6\text{O}_5$, is produced when a concentrated aqueous solution of tetronic acid is heated on the water bath, and allowed to remain at ordinary temperatures during one or two weeks; it is much less readily soluble in water than tetronic acid, and crystallises in aggregates of white needles, which contain $1\text{H}_2\text{O}$. It becomes yellow at 240 — 245° , and melts at 263° , at which temperature it decomposes completely. The aqueous solution develops a red coloration with ferric chloride, and becomes yellow with sodium nitrite, or reddish-brown if the solution is concentrated. The barium salt crystallises in slender needles containing $5\text{H}_2\text{O}$, and dissolves readily in water; the calcium salt also contains $5\text{H}_2\text{O}$, and crystallises in needles, being less readily soluble than the barium salt.

M. O. F.

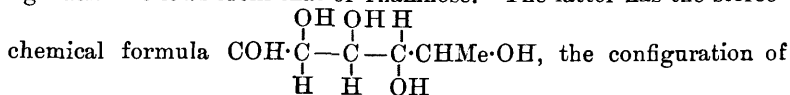
Hydroxytrimethylsuccinic acid. By KARL AUWERS and G. VON CAMPENHAUSEN (*Ber.*, 1896, **29**, 1543—1549).—*Hydroxytrimethylsuccinic acid*, $\text{COOH}\cdot\text{CMe}_2\cdot\text{CMe}(\text{OH})\cdot\text{COOH}$, is obtained from the cyanhydrin of ethylic dimethylacetoacetate; an ethereal solution of this substance is poured on to a large excess (five times the theoretical amount) of powdered potassium cyanide, just moistened with water, and strong hydrochloric acid is added, drop by drop, in amount equivalent to the cyanide. After 24 hours, the ethereal solution is poured into three times its volume of strong hydrochloric acid, filtered after 24 hours, then heated for several hours on the water bath, and finally evaporated to dryness, the residue being extracted with ethylic acetate. It melts at $153\text{--}154^\circ$ when heated slowly, at $159\text{--}160^\circ$ when heated quickly; at a higher temperature, it appears to form the anhydride, which distils over at about 240° . With acetic chloride, it yields the *acetyl* derivative, not of the acid, but of the *anhydride*; this melts at $67\text{--}68^\circ$. With aniline, it yields an *anil* melting at $145\text{--}146^\circ$; with paratoluidine, the corresponding *tolil*, $\text{CMe}_2\cdot\text{CO}\text{---}$
 $\text{CMe}(\text{OH})\cdot\text{CO} > \text{N}\cdot\text{C}_6\text{H}_4\text{Me}$, melting at $184\text{--}185^\circ$; this yields, with acetic chloride, an *acetyl* derivative melting at 131° , which, when heated with alcoholic potash, does not lose its acetyl group, but yields the *acetyl* derivative of the *tolilic acid*,



which melts at $156\text{--}157^\circ$ when heated slowly, at 160° when heated quickly (at which end of the chain the tolylamido-group is situated is, of course, uncertain). When strong alcoholic potash (20 per cent.) is used, a substance, melting at $108\text{--}108.5^\circ$, and insoluble in alkalis and acids, is obtained; and G. Komppa, who is also engaged in investigating hydroxytrimethylsuccinic acid, even seems to have obtained the normal product of hydrolysis, the *tolil*. The acetyltolilic acid, after it has been melted and allowed to solidify again in a melting-point tube, then melts at 185° , being, apparently, converted into the *tolil*; if, however, a larger quantity is heated for a short time above its melting point, the acetyltolyl, melting at 131° , is obtained.

C. F. B.

The Configuration of Dextrotartaric acid. By EMIL FISCHER (*Ber.*, 1896, **29**, 1377—1383).—The formula of dextrotartaric acid, with reference to the formulæ employed for the various members of the sugar group, can be ascertained by converting rhamnose, the constitution of which with reference to that of the glucoses is known, into methyltetrose by Wohl's method, and then treating the latter with nitric acid. Dextrotartaric acid is thus produced, and its configuration follows from that of rhamnose. The latter has the stereo-



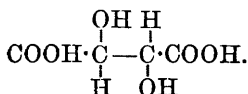
the groups combined with the δ -carbon atom being unknown (*Abstr.*, 1894, i, 218).

Tetracetylramnonic nitrile, $\text{CH}_3\cdot[\text{CH}\cdot\text{OAc}]_4\cdot\text{CN}$, is obtained by treating the oxime with acetic anhydride and sodium acetate. It is

moderately soluble in hot water, crystallises from alcohol in large, transparent crystals, and melts at 69—70°. When it is treated with an ammoniacal solution of silver oxide, it yields the *acetamide compound of methyltetrose*, $\text{CH}_3\cdot[\text{CH}\cdot\text{OH}]_3\cdot\text{CH}(\text{NHAc})_2$, which crystallises from water in colourless prisms, and melts at 201—205° (corr.); it does not reduce Fehling's solution. *Methyltetrose* forms slender, yellow needles, and melts somewhat indefinitely between 171° and

174° (uncorr.). It has the configuration
$$\begin{array}{c} \text{OH} \quad \text{H} \\ | \quad | \\ \text{COH}\cdot\text{C}-\text{C}\cdot\text{CHMe}\cdot\text{OH}, \\ | \quad | \\ \text{H} \quad \text{OH} \end{array}$$

as is shown by its formation from rhamnose. When methyltetrose or its acetamide compound is treated with nitric acid, it yields dextro-tartaric acid, which must, therefore, have the configuration



This oxidation of methyltetrose with formation of dextrotartaric acid is precisely similar to the formation of *l*-trihydroxyglutaric acid from rhamnose, and of mucic acid from rhamnohexonic acid.

It follows from the configuration of *d*-tartaric acid that the formula of the malic acid produced from it by the action of hydriodic acid,

must be
$$\begin{array}{c} \text{OH} \\ | \\ \text{COOH}\cdot\text{C}\cdot\text{CH}_2\cdot\text{COOH}, \\ | \\ \text{H} \end{array}$$
 whilst that of the corresponding as-

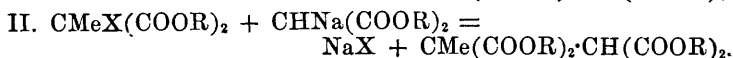
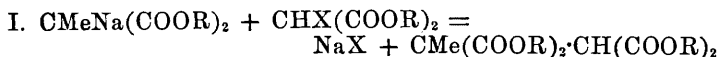
partic acid must be
$$\begin{array}{c} \text{NH}_2 \\ | \\ \text{COOH}\cdot\text{C}\cdot\text{CH}_2\cdot\text{COOH}. \\ | \\ \text{H} \end{array}$$

This formula for *d*-tartaric acid is also in complete agreement with the fact that *d*-saccharic acid yields *d*-tartaric acid on oxidation (Fischer and Crossley, *Abstr.*, 1894, i, 230). A. H.

Racemism. XIV. By ISIDOR TRAUBE (*Ber.*, 1896, 29, 1394—1397).—The application of the molecular volumetric method of determining molecular weights to optically active and inactive substances shows that in every case which has been examined, the three forms, dextro- and lævo-rotatory, and racemic, all have approximately the same molecular weight. In the case of substances such as hydrocarbons, ethereal salts, and ethers, they are all monomolecular, and the racemic form must be looked on as a mixture of the two optically opposed forms. This is the case with the ethylic tartrates, *d*- and *l*-limonene and dipentene, and the three carvones. Dextrotartaric acid and racemic acid, on the other hand, have both of them the double molecular weight, and it is probable that the formation of racemic acid from dextro- and lævo-tartaric acids, is represented by the equation $dd + ll = 2dl$. In other cases, the average molecular weight appears to be intermediate between those corresponding with the single and the double formula. For isoamylic alcohol it has the ratio 1.52 to the single formula; whilst with coniine the ratio is 1.6.

A. H.

Formation of Carbon Chains. X. Condensations which should yield an Ethereal Salt of Methylacetylenetetracarboxylic [1:1:2:2-Propanetetracarboxylic] acid. By CARL A. BISCHOFF (*Ber.*, 1896, **29**, 1504—1514).—Ethylic propanetetracarboxylate should be formed as the normal product of the following reactions.



R being either a methyl or an ethyl group and X a chlorine or bromine atom.

(1) In the first case, namely, in the condensation of methylic sodiomethylmalonate and methylic chloromalonate, the chief products isolated were methylic ethanetetracarboxylate and the unsaturated methylic ethylenetetracarboxylate, from which succinic and fumaric acids respectively were produced. Methylsuccinic acid, which would have been produced from any methylic propanetetracarboxylate formed, could not be isolated.

This reaction is, therefore, abnormal, 2 mols. of methylic sodiomethylmalonate condensing with 2 mols. of the chloro-compound with the formation of the unsaturated methylic ethylenetetracarboxylate and regeneration of methylic methylmalonate; at the same time 3 mols. of the methylic chloromalonate react with 3 mols. of sodium methoxide with the production of methylic ethanetetracarboxylate and methylic dimethoxymalonate.

(2) The condensation between methylic sodiomethylmalonate and methylic bromomalonate also proceeds abnormally, a trace of the normal product, however, being produced; the reaction otherwise proceeds somewhat differently to that of the chloro-compound, the methylic bromomalonate being, for the most part, converted into the methylic propanehexacarboxylate.

Employing the ethylic salts instead of the methylic in the previous experiments, the reaction between ethylic sodiomethylmalonate and ethylic chloromalonate was found to proceed abnormally; with the bromo-compound, a certain quantity of the normal product was, however, isolated.

The condensation between ethylic sodiomalonate and ethylic chloromethylmalonate also yielded none of the normal product, whilst with ethylic bromomethylmalonate a product was obtained which yielded propanetricarboxylic acid on hydrolysis, and was evidently the normal condensation product, ethylic propanetetracarboxylate.

J. F. T.

Formation of Carbon Chains. XI. Condensations which should yield an Ethereal Salt of Ethylacetylenetetracarboxylic [1:1:2:2-Butanetetracarboxylic] acid. By CARL A. BISCHOFF (*Ber.*, 1896, **29**, 1514—1521).—The condensation between ethylic bromomalonate and ethylic sodethylmalonate, both in alcoholic and in xylene solutions, yields ethylic ethylenetetracarboxylate, the corresponding chloro-compound, however, only gives this product

in alcoholic solution, whilst in xylene, ethylic ethanetetracarboxylate is formed. Condensations between ethylic sodiomalonate and ethylic chlorethylmalonate, ethylic sodiomalonate and ethylic bromomalonate, ethylic sodethylmalonate and ethylic chloro- and bromomalonates (in both alcohol and xylene), were in no case found to yield the normal product.

J. F. T.

Synthesis of Carbamide and symmetrical complex Carbamides. By PAUL CAZENEUVE (*Compt. rend.*, 1896, **122**, 999—1000).—When guaiacol carbonate is mixed with alcohol of 93° saturated with ammonia, it is rapidly converted into carbamide with liberation of guaiacol. The reaction is analogous to that of ammonia on ethylic carbonate, and it confirms the view that the guaiacol carbonate, $\text{CO}(\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{OMe})_2$, has the function of an ethereal salt.

Similarly, guaiacol carbonate yields diphenylcarbamide when heated with aniline, and the corresponding symmetrical carbamides when heated with orthotoluidine and paratoluidine.

C. H. B.

α -Dialkylhydantoïns. By GIORGIO ERRERA (*Gazzetta*, 1896, **26**, i, 197—211).—On treating cyanacetamide in alcoholic solution with sodium ethoxide, the two methylenic hydrogen atoms are displaced by sodium, and a crystalline, white *disodio*-derivative is deposited; the latter, when treated with an alkylic iodide, yields an α -dialkylcyanacetamide, which is acted on in a twofold manner by alkaline hypobromite; the CN group is hydrated, and becomes a $-\text{CO}\cdot\text{NH}_2$ group, whilst the original $-\text{CO}\cdot\text{NH}_2$ is oxidised to the isocyanic group $-\text{NCO}$, in accordance with Hofmann's reaction. The reaction, however, does not end with the formation of the compound $\text{CONH}_2\cdot\text{CR}_2\cdot\text{NCO}$ from $\text{CN}\cdot\text{CR}_2\cdot\text{CONH}_2$, but the amido and isocyanic

groups join to form the hydantoïn derivative, $\text{CR}_2\cdot\text{C}\begin{smallmatrix} \text{CO}\cdot\text{NH} \\ \text{NH}\cdot\text{CO} \end{smallmatrix}$. Hydantoïn itself cannot be prepared by the action of hypobromite on cyanacetamide, because the methylene group becomes attacked and the molecule splits up.

Dibenzylcyanacetamide, $\text{CN}\cdot\text{C}(\text{CH}_2\text{Ph})_2\cdot\text{CONH}_2$, is readily obtained by heating cyanacetamide, to which sodium ethoxide has been added, with benzyl chloride on the water bath; it crystallises in colourless, rhombic tablets melting at 165°, and is soluble in hot alcohol; $a : b : c = 0\cdot2880 : 1 : 0\cdot30674$. On fusion with dehydrating agents, such as phosphoric anhydride, it yields the nitrile of dibenzylmalonic acid, whilst, if the finely powdered amine is heated at 100° with a potash solution of bromine, it is converted into

α -dibenzylhydantoïn, $(\text{CH}_2\text{Ph})_2\text{C}\begin{smallmatrix} \text{CO}\cdot\text{NH} \\ \text{NH}\cdot\text{CO} \end{smallmatrix}$, which can be purified by

dissolving in soda and precipitating the filtered solution with acid. It crystallises in lustrous, colourless laminæ, melting at 208—209°, and dissolves in caustic alkalis, but not in alkaline carbonates. Its

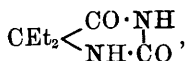
dinitro-derivative, $(\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2)_2\text{C}\begin{smallmatrix} \text{CO}\cdot\text{NH} \\ \text{NH}\cdot\text{CO} \end{smallmatrix}$, is obtained by boiling with fuming nitric acid, and crystallises in yellow laminæ melting

and decomposing at 285° ; the nitro- and methylene-groups are probably in the para-position.

α -Tetrabromodibenzylhydantoin, $(\text{C}_6\text{H}_3\text{Br}_2\cdot\text{CH}_2)_2\text{C} < \begin{smallmatrix} \text{CO}\cdot\text{NH} \\ \text{NH}\cdot\text{CO} \end{smallmatrix}$, obtained by direct bromination in presence of iodine, crystallises in white laminæ melting at 285° ; it dissolves readily in caustic alkalis, and is possibly a mixture of isomerides.

Dipropylcyanacetamide, $\text{CN}\cdot\text{CPr}_2\cdot\text{CONH}_2$, prepared with the aid of propylic bromide, forms white crystals melting at 152 – 153° ; alkaline hypobromite readily converts it into α -dipropylhydantoin, $\text{CPr}_2 < \begin{smallmatrix} \text{CO}\cdot\text{NH} \\ \text{NH}\cdot\text{CO} \end{smallmatrix}$, which crystallises in colourless laminæ melting at 199° .

Diethylcyanacetamide, $\text{CN}\cdot\text{CEt}_2\cdot\text{CONH}_2$, prepared with the aid of ethylic iodide, forms irregular, colourless crystals melting at 121° ; with alkaline hypobromite, it yields α -diethylhydantoin,



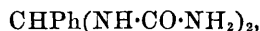
which crystallises in large, colourless, rhombic prisms melting at 165° ; $a : b : c = 0.83910 : 1 : 2.51715$.

Dimethylcyanacetamide, $\text{CN}\cdot\text{CMe}_2\cdot\text{CONH}_2$, crystallises in colourless, triclinic laminæ melting at 105 – 106° ;

$$a : b : c = 1.065485 : 1 : 1.18805.$$

$\alpha = 76^{\circ} 42'$, $\beta = 50^{\circ} 8'$, $\gamma = 67^{\circ} 33'$. The α -dimethylhydantoin obtained from it melts at 173 – 174° , not at 175° , as Urech's preparation did (Abstr., 1873, 59). W. J. P.

Benzylidenebiuret and Allied Compounds. By HUGO SCHIFF (*Annalen*, 1896, 291, 367–377).—Benzylidenedicarbamide,



is produced by heating carbamide with benzaldehyde; it melts at 200° , and when heated at 220 – 230° , yields benzaldehyde, water, ammonia, and ammonium carbonate, the residue consisting of cyanuric acid and benzylidenebiuret (compare Abstr., 1894, i, 374).

Benzylidenemethylbiuret, which probably has the constitution $\text{NMe} < \begin{smallmatrix} \text{CO}\cdot\text{NH} \\ \text{CO}\cdot\text{NH} \end{smallmatrix} > \text{CHPh}$, is obtained by heating benzylidenebiuret in a reflux apparatus with alkali and the alkylic iodide, although biuret does not yield alkyl derivatives under these conditions; it separates from water in colourless, prismatic needles, and melts at 238° . Benzylideneethylbiuret crystallises from water, and melts at 250° .

Benzylidenebismethylcarbamide, $\text{CHPh}(\text{NH}\cdot\text{CO}\cdot\text{NHMe})_2$, is produced on adding a few drops of concentrated hydrochloric acid to an alcoholic solution of methylcarbamide and benzaldehyde; it crystallises in needles, and melts at 187 – 188° . When heated at 250° , it yields methylamine, ammonia, ammonium carbonate, benzaldehyde,

and water, a small quantity of benzylidenemethylbiuret being also produced.

Hofmann observed the formation of dimethylcyanuric acid on distilling methylacetylcarbamide; the substance is also produced when methylcarbamide is heated with benzaldehyde at 220°. It is probable that trimethylcyanuric acid is formed at the same time.

According to the statement of Wilm and Wischin (*Annalen*, 1868, 147, 155), carbamide unites with ethylic chlorocarbonate, forming ethylic allophanate; the reaction, however, is not a simple one. When a mixture in molecular proportion is heated in a reflux apparatus during two or three hours, one-third of the salt undergoes no change; a crystalline solid is produced composed of cyanuric acid and ammonium chloride along with a trace of biuret, but no ethylic allophanate is formed. When double the proportion of carbamide is employed, it yields one-sixth of its weight of ethylic allophanate, along with cyanuric acid, ammonium chloride, and a very small quantity of biuret.

Carbonyldicarbamide, $\text{CO}(\text{NH}\cdot\text{CO}\cdot\text{NH}_2)_2$, is formed when carbamide is heated with a 20 per cent. solution of carbonyl dichloride in toluene, the temperature being maintained at 100° during two days; it crystallises from water in lustrous scales, and melts at 231—232°. Further treatment with carbonyl dichloride gives rise, as Schmidt has pointed out, to cyanuric acid, and carbonyldibiuret is produced in the same way (compare Archdeacon and Cohen (*Proc.*, 1895, 148).

Determinations of the solubility of cyanuric acid are given; one part of the anhydrous acid dissolves in about 800 parts of water at ordinary temperatures.

M. O. F.

Acetylbiuret and Benzoylbiuret. By ADRIANO OSTROGOVICH (*Annalen*, 1896, 291, 377—380).—*Acetylbiuret*,

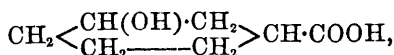


is obtained when anhydrous biuret and acetic chloride are heated during one hour in sealed tubes at 100°; it crystallises from water in flat, nacreous needles, and melts at 193—193.5°. The substance is also formed on heating carbamide with acetylurethane (compare this vol., i, 261). An attempt to produce this substance by the action of ammonia on ethylic acetylallophanate at 50° resulted in the formation of ethylic allophanate and acetamide; when alcoholic ammonia is employed, and the temperature raised to 100°, biuret and acetamide are produced.

Benzoylbiuret separates from boiling water as a colourless, crystalline powder, and melts and decomposes at 228—230°. Concentrated alcoholic or aqueous ammonia at 40—50° converts ethylic benzoylallophanate into ethylic allophanate and benzamide, whilst, at 100°, benzamide and biuret are produced.

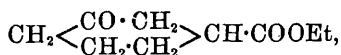
M. O. F.

Reduction of Phenolcarboxylic acids. II. By ALFRED EINHORN [and FRANZ COBLITZ] (*Annalen*, 1896, 291, 297—304; compare this vol., i, 45).—3:1-*Hydroxyhexamethylenecarboxylic acid*,



is obtained by slowly adding sodium to a boiling solution of meta-hydroxybenzoic acid in absolute alcohol, and crystallises from ethylic acetate in leaflets melting at 132° ; the *barium* salt contains $1\text{H}_2\text{O}$, and the *copper* salt is a green powder, dissolving readily in water and alcohol. The *methylic* and *ethylic* salts are colourless liquids of agreeable odour, boiling at $140\text{--}150^\circ$ and $148\text{--}158^\circ$ respectively under a pressure of 14 mm.; the *amide* crystallises from water in white leaflets, and melts at 161° . When diazobenzene chloride (2 mols.) is added to an aqueous solution of the sodium salt, the compound $\text{C}_{18}\text{H}_{16}\text{N}_4\text{O}$, is produced; it crystallises from alcohol in lustrous, red needles, and melts at 131° , dissolving in concentrated sulphuric acid, with development of a dark red coloration.

Ethylic 3 : 1-ketohexamethylenecarboxylate,



is formed when ethylic 3 : 1-hydroxyhexamethylenecarboxylate is oxidised with sodium dichromate and sulphuric acid; it is a colourless liquid of agreeable odour, and boils at $170\text{--}180^\circ$ under a pressure of 16 mm. Hydrolysis gives rise to the acid, which has been already obtained by von Baeyer and Tutein on eliminating carbonic anhydride from hydroxytetrahydroterephthalic acid (Abstr., 1889, 1180). M. O. F.

Action of Bromine on Aromatic Iodo-compounds. By H. HIRTZ (*Ber.*, 1896, 29, 1404—1411).—When bromine acts on aromatic iodo-compounds, the iodine is seldom replaced by bromine, as is the general rule in the aliphatic series, and there is no formation of additive compounds (iododibromides), as is the case when chlorine is used; in the majority of cases a simple substitution product is formed.

Bromine acts on iodobenzene in much the same manner as on benzene itself, and forms 1 : 4-bromiodobenzene. Pariodotoluene is but slowly attacked by bromine, and even when excess of halogen is used, the action is still incomplete; the product, 2 : 4-bromiodotoluene, $\text{C}_7\text{H}_6\text{BrI}$, is an oil boiling at $250\text{--}265^\circ$ (uncorr.), which, on dissolution in cold, fuming nitric acid, yields a 2 : 4 : 2-bromiodonitrotoluene, $\text{C}_7\text{H}_5\text{BrI} \cdot \text{NO}_2$; this crystallises from alcohol in bright yellow needles, and melts at 92° . Metiodotoluene is rapidly acted on by bromine, and the reaction must be carried out at as low a temperature as possible; the product is an oil, which boils at $255\text{--}265^\circ$ (uncorr.), and, when heated with a mixture of fuming nitric and sulphuric acids, yields a bromometiododinitrotoluene, $\text{C}_7\text{H}_4\text{BrI}(\text{NO}_2)_2$, which crystallises from acetic acid, and forms fine, bright yellow needles, melting at $139\text{--}141^\circ$. With regard to its behaviour towards bromine, orthiodotoluene is intermediate in character between the meta- and para-compounds, the interaction taking place somewhat readily with the production of a bromiodotoluene [probably 2 : 4] boiling at $262\text{--}266^\circ$.

Pariodobenzoic acid is not attacked at ordinary temperatures, but at a temperature of $160\text{--}180^\circ$ the iodine is replaced by bromine;

whilst at 125° the replacement is only partial, and the two acids present may be separated by converting the iodo-compound into the iododichloride, which is insoluble in acetic acid. Under no conditions does the bromine act as a substituting agent. The behaviour of metiodobenzoic acid closely resembles that of the para-acid. Ortho-iodobenzoic acid, however, yields a mixture of substances which, by the action of chlorine, yields the orthiododichloride of parabromobenzoic acid; the mother liquor from the latter substance, when treated with caustic soda, yields the sodium salts of orthiodosobenzoic acid and a mixture of several bromobenzoic acids.

Bromine acts with explosive energy on α -iodonaphthalene, yielding bromiodonaphthalene [probably 1 : 4], melting at 85·5°. β -Iodonaphthalene is also violently attacked, and yields a mixed product; the latter, on treatment with chlorine, affords an iododichloride, which on reduction gives a *bromo- β -iodonaphthalene*, which crystallises from dilute alcohol, and melts at 55°; the mother liquor from the iodochloride yields a dark oil, which deposits white crystals of 1 : 2-bromiodonaphthalene.

Ortho- and para-iodoanisols have their iodine replaced by bromine when treated with that substance; the product in both cases is 2 : 4-dibromoanisol; the latter, when dissolved in cold, fuming nitric acid, yields a 2 : 4-*dibromonitroanisol*, $\text{OMe}\cdot\text{C}_6\text{H}_2\text{Br}_2\cdot\text{NO}_2$, which crystallises from dilute alcohol in long, silky, yellowish needles, and melts at 116—117°. If, before bromination, pariodoanisol be diluted with five times its weight of chloroform, the product is 2 : 4-*bromiodoanisol*, melting at 89°. Orthoiodoanisol, under similar conditions, yields 4 : 2-*bromiodoanisol*, melting at 68°; both substances form large, white, rhombic tables, and crystallise with great readiness.

Metiodoanisol, $\text{OMe}\cdot\text{C}_6\text{H}_4\text{I}$, is readily prepared from metiodophenol; it forms an oil, which is readily soluble in alcohol and ether, and has an odour recalling that of iodobenzene and not that of anisol; it boils at 244—245° (corr.); it is attacked by bromine with even greater energy than the corresponding ortho- and para-derivatives, but the iodine is not displaced; the product is a *bromiodoanisol*,



and forms an oil, which boils and decomposes at 285—295° at the ordinary pressure, but may be distilled without alteration in a vacuum, its boiling point then being 163—164°; it does not give a solid nitro-derivative, but when treated with chlorine and then reduced, it yields a *chlorobromiodoanisol*, $\text{OMe}\cdot\text{C}_6\text{H}_2\text{ClBrI}$, which separates from alcohol in snow-white crystals, melting at 111—112°. A. L.

Rational Methods for preparing Iodoxy-Compounds. By H. CONRAD C. WILLGERODT (*Ber.*, 1896, 29, 1567—1575).—The method of preparing an aromatic iodoxy-compound, $\text{R}\cdot\text{IO}_2$, by heating the corresponding iodoso-compound, $\text{R}\cdot\text{IO}$, is not satisfactory, because half of the latter goes back into the state of the iodo-compound, $\text{R}\cdot\text{I}$. The author has found that it is possible to obtain the iodoxy-compound by the use of an oxidising agent, and thus avoid this loss. Many methods were tried; the iodoso-compound was directly oxidised

with "hypochlorous acid" (prepared by saturating bleaching powder solution with carbonic anhydride, and filtering), with bleaching powder solution, or with sodium hypochlorite (from bleaching powder and sodium carbonate); or the iododichloride, $R \cdot ICl_2$, was oxidised with sodium hypochlorite, or with bleaching powder solution; or the iodo-compound was chlorinated in aqueous solution, sodium hydroxide added to the iododichloride so formed, and more chlorine passed in, or it was oxidised with "hypochlorous acid," or with sodium hypobromite. In all cases the iodoxy-compound was obtained, and in many of them the yield was quantitative. The method which, on the whole, the author seems to regard as the most trustworthy, is the oxidation of the iododichloride with bleaching powder solution. Iodoxybenzene, parachloriodoxybenzene, paraiodoxytoluene, and β -iodoxynaphthalene were prepared in this way. The last is a new substance; it detonates at 200° when pure; in its preparation β -iodophthalic acid was obtained as a bye-product. C. F. B.

New Methods of Research in Organic Chemistry. By WALTER LÖB (*Ber.*, 1896, **29**, 1390—1392).—Many reactions which occur under the influence of an electric current can be carried out in a convenient manner by so arranging the reacting substances that they make up a galvanic element. Thus when a porous cell filled with a solution of nitrobenzene in concentrated sulphuric acid is put into a solution of dilute sulphuric acid, a piece of platinum placed in the nitrobenzene solution, and a piece of zinc in the dilute sulphuric acid, and the two metals then connected, the nitrobenzene is rapidly and completely reduced to amidophenol. In a similar manner orthonitrobenzoic acid dissolved in an alkali may be reduced to azoxy- and hydrazo-benzoic acid. Many other reactions can be carried out in a similar way.

A. H.

Derivatives of Phenyllic Ether. By CARL HAEUSSERMANN and H. TEICHMANN (*Ber.*, 1896, **29**, 1446—1450).—*Para-* and *ortho-nitrophenylic ether*, $C_6H_5 \cdot O \cdot C_6H_4 \cdot NO_2$, were prepared by heating the corresponding chloronitrobenzenes with potassium phenoxide and phenol at 150° . They yield hydrazo-compounds when reduced with zinc dust and alcoholic potash, and these are oxidised by a current of air, or by ferric chloride, into azo-compounds. When reduced with tin and alcoholic hydrogen chloride, paranitrophenyl ether yields an imido-ether. Potassium paranitrophenoxide does not react so readily; in order to get a dinitrophenyl ether, it has to be brought in small quantities into a large excess of 1 : 4-chloronitrobenzene kept at a temperature of 225 — 235° .

The following compounds were prepared; the numbers indicate melting points, except where otherwise stated. *Nitrophenylic ethers*: *para-*, 61° , boils at 320° ; *ortho-*, boils at 205° under 45 mm. pressure, sp. gr. = 1.258 at 15° . *Parahydrazophenylic ether*, yellowish, 116° (impure). *Azophenylic ethers*: *para-*, orange, 149.5 — 150° ; *ortho-*, red, 168 — 169° . *Paramidophenylic ether*, stable in air, 84° (acetyl derivative, 127°). *Diparanitrophenylic ether*, yellowish, 142.5 — 143° , probably identical with the substance obtained by Hoffmeister (*Annalen*, **159**, 207) in the nitration of phenyl ether. *Diparamidophenylic ether*,

186—187° (Hoffmeister, 185°); the *hydrochloride* crystallises with H_2O ; yields azo-dyes that may possibly have a commercial value. A *orthoparadinitrophenylic ether*, $O(C_6H_4 \cdot NO_2)_2$, 103·5°, has also been obtained. C. F. B.

Chemical Constitution and Oxidisability in presence of Laccases. By GABRIEL BERTRAND (*Compt. rend.*, 1896, **122**, 1132—1133).—In the case of dihydric and trihydric phenols, amidophenols, and diamidobenzenes, the ortho- and para-derivatives are readily oxidised by oxygen or air in presence of laccase, whilst the meta-derivatives are not. Pyrocatechuic acid, gallic acid, and hexahydric phenol, $C_6(OH)_6$, are also readily oxidised. The rate of oxidation seems to depend on the tendency of the particular compound to form a quinone, and the general conclusion is that laccase acts most readily, if not exclusively, on compounds of the benzene series which contain not fewer than two hydroxyl or amidogen groups in the ortho- or para-position (compare Abstr., 1895, i, 386). C. H. B.

Action of Ethylic Orthoformate on Primary Aromatic Amines. By REINHOLD WALTHER (*J. pr. Chem.*, 1896, [2], **53**, 472—478).—This paper contains the details of the work which has already been summarised in this vol., i, 165. A. G. B.

Stereochemistry of Nitrogen Compounds. By WILHELM VON MILLER and JOSEF PLÖCHL [with G. MOZDZYNSKI (*Ber.*, 1896, **29**, i, 1462—1472)].—If xyloidine [$Me_2 : NH_2 = 1 : 3 : 4$] is dissolved in dilute hydrochloric acid, acetaldehyde added, and the mixture allowed to remain for 24 hours, condensation takes place, and a mixture of two isomeric substances, $C_6H_3Me_2 \cdot NH \cdot CHMe \cdot CH_2 \cdot CHO$, is eventually obtained. The one crystallises in long, triclinic prisms, melts at 131°, and is sparingly soluble in the ordinary solvents, the other crystallises in short, monoclinic prisms having the appearance of rhombohedra, melts at 102°, and is readily soluble. On crystallising the mixture, however, the substance of higher melting point first separates, and then a mixture of the two substances, from which that of lower melting point can only be isolated by picking out its crystals with the aid of a lens. Each substance yields a nitroso-derivative, and both yield the same *benzoyl* derivative; the latter melts at 157°, and from it the isomeride melting at 131° is regenerated. Further, both yield the same *oxime*, melting at 165°, and they also condense with aromatic amines, NH_2R , yielding compounds

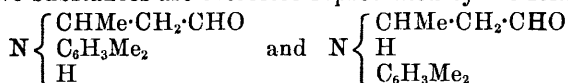


the aniline, anisidine, and 1 : 3 : 4 xyloidine compounds melt at 95°, 118—119°, and 147° respectively; from the last compound, the substance of melting point 102° is regenerated when it is allowed to remain with hydrochloric acid. This compound is also the direct product of condensation when aldehyde and xyloidine, suspended in much water, are warmed together at 70°. Yet another condensation product, melting at 55—60°, has been obtained, but it has not been investigated.

The two aldehyde bases are obviously stereoisomeric; they have

different physical properties, but react chemically in the same way. As indicated above, the isomeride melting at 102° can be converted into the other by passage through the benzoyl derivative, and the reverse transformation can be effected by means of the xylidine derivative; the isomeride of lower melting point is also partly converted into the other, when it is recrystallised, warmed with water, heated above its melting point, &c. The isomerism cannot be due to the asymmetric carbon atom, for both substances are optically inactive. It is a *stereoisomerism of a new kind*, and must be regarded as due to the different arrangement, in one plane, of the groups united to the nitrogen atom.

The two substances are therefore represented by the formulæ



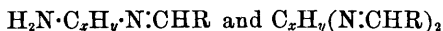
The first formula is assigned to the compound melting at 102° , because it readily yields a quinaldine when heated above its melting point or when boiled with hydrochloric acid, and must therefore contain the aldehyde group and the benzene ring in closer proximity than is the case with its isomeride, which yields hardly any quinaldine under similar circumstances.

C. F. B.

Thiodiphenylamine. By OSKAR UNGER and KARL A. HOFMANN (*Ber.*, 1896, 29, 1362—1368; compare *Abstr.*, 1895, i, 132).—Thiodiphenylamine hydrochloride is deposited in colourless, slender needles when the amine, dissolved in alcohol, is saturated with hydrogen chloride and cooled to 0° . Mono-, di-, and tetra-chlorothiodiphenylamines are obtained together by dissolving the amine in anhydrous ether containing 3—4 per cent. of hydrogen chloride, and treating the well-cooled solution with the oxides of nitrogen evolved from arsenious anhydride and nitric acid (sp. gr. = 1.3); the amine may also be dissolved in ether, treated with nitric oxides, and the resulting product heated with alcoholic hydrogen chloride; the former method gives all three compounds, the latter chiefly the tetrachloro-derivative. The best yield of the mono- and dichloro-compounds is obtained by dissolving the amine (3 parts) in alcoholic hydrogen chloride, and adding sodium nitrite (1 part) dissolved in a little water, the temperature is maintained at 0° during about an hour, and finely divided copper is added. *Tetrachlorothiodiphenylamine*, $\text{C}_{12}\text{H}_5\text{NSCl}_4$, is sparingly soluble in alcohol; it is formed, together with the blue compound previously described (*loc. cit.*), by heating with aniline and aniline hydrochloride the substance formed by the action of nitric oxides on the amine in ethereal solution, and, in small quantity, by the action of chlorine on the amine in chloroform solution at 30° ; it crystallises from benzene in pale yellow, slender needles melting at 235° . It is not changed by concentrated sulphuric acid at the ordinary temperature, but when warmed, a deep violet solution is obtained which has a well-defined absorption band, the maximum being at $\lambda = 596$. With concentrated nitric acid, the tetrachloramine evolves chlorine and yields a nitro-derivative, with nitric acid diluted with glacial acetic acid, an oxidation product, probably

$C_{12}H_5NSCl_4O$, is formed; this crystallises in red, lustrous prisms, and does not yield a dye when reduced. These reactions indicate that the chlorine occupies in both nuclei the positions 2 : 4. Mono- and di-chlorothiodiphenylamine are readily soluble in alcohol; when diluted and the product crystallised from benzene, greenish, silvery, lustrous plates are obtained which consist of an isomorphous mixture containing 2 mols. of the dichloro-compound : 5 mols. of the mono-chloride; the substances are separated by repeated crystallisation from benzene and alcohol. *Dichlorothiodiphenylamine*, $C_{12}H_7NSCl_2$, crystallises from alcohol in slender, colourless plates, of silvery lustre, melting and decomposing at $225-227^\circ$; it becomes green when exposed to air, and dissolves in concentrated sulphuric acid with an intense cherry-red colour; the solution has a broad absorption band in the green, the maximum being at $\lambda = 569$. The molecular weight, determined by the ebullioscopic method, agrees with the formula. By the action of nitric acid, *dinitrodichlorodiphenylsulphoxide*, $C_{12}H_5(NO_2)_2NCl_2SO$, is formed; it crystallises in yellow needles, and, when reduced by means of stannous chloride and hydrochloric acid, yields leucoisothionine; the nitro-groups, and therefore also the chlorine atoms, probably occupy the positions 2 : 4, $NH = 1$. An isomeric *dichlorothiodiphenylamine* is obtained in very small quantity, together with the tetrachloro-compound, by the direct action of chlorine on the amine; it crystallises in pale, grass-green prisms, melts at 222° , and when nitrated and reduced, yields no dye, indicating that both chlorine atoms are in the para-position. *Chlorothiodiphenylamine*, $C_{12}H_5NSCl$, could not be completely purified; in general properties it closely resembles the dichloro-derivative, its characteristic absorption band attains a maximum at $\lambda = 544$. The compounds formed by the action of hydrogen chloride and nitric oxides respectively on thiodiphenylamine (see above) are amorphous and too unstable to purify; the former evolves 60—70 per cent. of its chlorine as hydrogen chloride when it is heated at 100° , the ratio $N : S : Cl = 1 : 1 : 1.2$; the nitric oxides appear to act as dehydrating agents, no nitrosamine or nitroso-derivative is formed, and all attempts to prepare the latter were fruitless. The action of hydrogen chloride on thiodiphenylamine and on quinone appear to be similar; in the latter case also an additive compound is formed and an intense coloration produced. J. B. T.

Action of Aldehydes on Aromatic Orthodiamines. IV. By OSCAR HINSBERG and P. KOLLER (*Ber.*, 1896, **29**, 1497—1504).—The condensation between aldehydes and aromatic orthodiamines appears to be of a general character. Compounds of the formulæ



being formed. The compounds produced by the condensation of ethylic acetoacetate and aromatic orthodiamines appear to have an analogous structure.

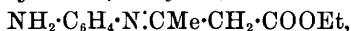
Benzylideneorthophenylenediamine, $H_2N \cdot C_6H_4 \cdot N : CHPh$, formed by the condensation of orthophenylenediamine with benzaldehyde (1 mol.), is a yellow, crystalline solid melting at $60-61^\circ$, after

recrystallisation from light petroleum (40—50°). It is readily converted into the imidazole melting at 280° by either heating alone at 100°, or by boiling its alcoholic or ethereal solution in the air; benzylideneorthophenylenediamine is in its mode of preparation and properties closely analogous to paranitrobenzylideneorthophenylenediamine (Hinsberg and Funcke, Abstr., 1894, i, 623).

Dibenzylideneorthophenylenediamine, $C_6H_4(N:CHPh)_2$, is formed when 2 mols. of benzaldehyde react with 1 mol. of orthophenylenediamine. It crystallises from light petroleum in yellow prisms melting at 106°, and it is soluble in alcohol, ether, and light petroleum, insoluble in water. By heating with dilute mineral acids, it is split up into benzaldehyde and orthophenylenediamine.

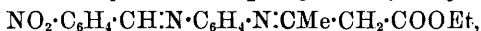
Benzylidene-1:2-naphthylenediamine, $NH_2 \cdot C_{10}H_6 \cdot N:CHPh$, prepared from 1:2-naphthylenediamine and benzaldehyde (1 mol.) forms yellow crystals melting at 156—157°. It is very stable, and remains unaltered on passing air through its boiling alcoholic solution. It, however, yields a derivative of the imidazole series (m. p. 210°) when dissolved in a solution of bromine in sodium hydroxide. Whether the N:C group is in the α - or β -position has not yet been determined. The corresponding dibenzylidene compound is not formed when 2 mols. of benzaldehyde react with 1 mol. of 1:2-naphthylenediamine in the cold; on warming, an imidazole base is produced.

Ethylic amidophenylimido- β -butyrate,



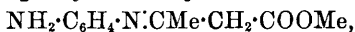
is produced by shaking finely divided orthophenylenediamine with an equivalent quantity of ethylic acetoacetate, and is purified by recrystallisation from light petroleum; it melts at 85°. An isomeric compound melting at 59° is also produced in this reaction; by repeated recrystallisation from light petroleum it passes into the substance melting at 85°. It is probably a substituted amidocrotonic acid, $NH_2 \cdot C_6H_4 \cdot NH \cdot CMc \cdot CH \cdot COOEt$.

Ethylic paranitrobenzylideneamidophenylimido- β -butyrate,



prepared from ethylic amidophenylimidobutyrate and paranitrobenzaldehyde (1 mol.) melts at 99°; it is decomposed by long boiling of its alcoholic solution.

Methylic orthamidophenylimidobutyrate,



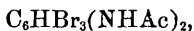
produced in the same way as the ethylic salt, crystallises from light petroleum in white needles melting at 87°.

Amidobenzaldehydine, $N \llcorner \begin{smallmatrix} C_6H_3(NH_2) \\ CPh \end{smallmatrix} \gg N \cdot CH_2Ph$, melts at 121°, and is obtained from 1:2:4-triamidobenzene and 2 mols. of benzaldehyde. It can be purified by dissolving in alcohol and precipitating by means of a concentrated solution of sodium chloride.

$\alpha\beta$ -Naphthobenzaldehydine, $N \llcorner \begin{smallmatrix} C_{10}H_6 \\ CPh \end{smallmatrix} \gg N \cdot CH_2Ph$, melts at 117°, and is formed by adding benzaldehyde to an acetic acid solution of 1:2-naphthylenediamine hydrochloride.

J. F. T.

Bromine Derivatives of Metaphenylenediamine. By C. LORING JACKSON and SIDNEY CALVERT (*Amer. Chem. J.*, 1896, **18**, 465—489).—*Tribromometaphenylenediamine* is prepared by passing a stream of air laden with bromine vapour into a solution of metaphenylenediamine, an excess of bromine being avoided. The precipitate is crystallised from alcohol, and assumes the form of long, slender, white, silky needles united longitudinally into ribbons with serrated ends. It melts at 158° , and dissolves freely in hot alcohol, ether, benzene, chloroform, glacial acetic acid, and carbon bisulphide, very slightly in light petroleum, and not in water. The diamine is a feeble base, but its *hydrochloride* was prepared by passing hydrogen chloride into a benzene solution of the base. By treating the diamine in benzene solution with acetic chloride, the *diacetamide*,



was prepared; it crystallises from hot glacial acetic acid in aggregates of small, white plates; it does not melt at 330° , and is very slightly soluble in all common solvents. *Tribromophenylenediurethane*, $\text{C}_6\text{HBr}_3(\text{NH}\cdot\text{COOEt})_2$, was prepared by boiling the diamine with ethylic chlorocarbonate; it crystallises in white needles, melts at 212° , and dissolves freely in hot alcohol, hot benzene, chloroform, and acetone, but not in light petroleum.

When tribromodinitrobenzene (m. p. 192° , made from symmetrical tribromobenzene) is reduced by zinc dust and acetic acid, it yields tribromophenylenediamine; but when the reduction is effected by tin and hydrochloric acid, all three bromine atoms are removed, metaphenylenediamine being produced. It was found that tribromophenylenediamine also parts with all its bromine when treated with tin and hydrochloric acid, but symmetrical tribromobenzene was unaltered by this treatment, although tribromaniline parted with a bromine atom in the ortho-position to the amido-group under the same conditions.

Metaphenylenediamine yields a tribromo-derivative when brominated, but metaphenylenediacetamide gives only *dibromometaphenylenediacetamide* when brominated in acetic acid solution, even though the bromine be in considerable excess. This compound crystallises in small, short prisms, melts and decomposes at $259\text{--}260^{\circ}$, and dissolves sparingly in alcohol, freely in benzene, chloroform, and glacial acetic acid, but not at all in ether and light petroleum. By hydrolysing the diacetamide with strong hydrochloric acid, a *dibromometaphenylenediamine* is obtained; it crystallises in white, slender needles, melts at 135° , and dissolves freely in alcohol, acetone, ether, hot chloroform and hot benzene, but only slightly in light petroleum and water; it forms salts more easily than the tribromo-derivative does, but is more difficultly debrominated; the *hydrochloride* and the *hydrobromide* are described.

The reduction of tetrabromodinitrobenzene by tin and hydrochloric acid in alcoholic solution yields *bromometaphenylenediamine* (? symmetrical), which crystallises in needles and monoclinic prisms, melts at $93\text{--}94^{\circ}$, and dissolves freely in acetone, alcohol, ether, and chloroform, slightly in benzene and carbon bisulphide, moderately in water,

and hardly at all in light petroleum; the *hydrobromide* is described. By bromination in ether, it yields *tetrabromometaphenylenediamine*, which crystallises in small, white needles, melts at $212-213^{\circ}$, and dissolves freely in benzene, chloroform, ether, acetone, carbon bisulphide, and hot alcohol, but very slightly in light petroleum; its basic properties are very feeble. A. G. B.

Oxidation Products of Orthamidodiphenylamine [Phenyl-orthophenylenediamine]. By OTTO FISCHER and A. DISCHINGER (*Ber.*, 1896, **29**, 1602—1608; compare *Abstr.*, 1893, i, 266).—In order to meet the criticism of Kehrman (*Abstr.*, 1895, i, 527), the authors have repeated the experiments of Fischer and Heiler on the oxidation of phenylorthophenylenediamine by means of ferric chloride (*Abstr.*, 1893, i, 266), and have confirmed their results. The chief product of the oxidation is anilidoaposafranine, which melts at $203-204^{\circ}$, and is identical with the compound prepared from aposafranine and aniline. When treated with alkalis, it yields anilidoaposafrone and hydroxyaposafranine, as found by Fischer and Heiler. This proves that the formula proposed by these chemists for anilidoaposafranine is the correct one. The anilidoaposafranine is accompanied by a second substance which probably has the composition $C_{36}H_{27}N_5$, and melts at $258-259^{\circ}$. This compound is probably formed by a secondary reaction between the anilidoaposafranine and phenyl-orthophenylenediamine. The presence of a small amount of this substance in the product obtained by Fischer and Heiler was the cause of the high melting point which these chemists ascribed to anilidoaposafranine.

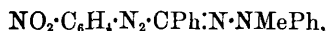
NOTE BY OTTO FISCHER AND EDUARD HEPP.—The formation of phenylfluorindine both from the oxidation product of phenylorthophenylenediamine and the anilidoaposafranine obtained synthetically, is a further proof of the accuracy of the formula proposed by Fischer and Heiler for the latter compound. Phenylfluorindine can be crystallised without change from ethylic benzoate if the solution be only boiled for a moment or two and then rapidly filtered (compare Kehrman and Bürgin, this vol., i, 512). A. H.

Symmetrical Triamidotoluene. By ARTHUR W. PALMER and WILLIAM C. BRENKE (*Ber.*, 1896, **29**, 1346—1347).—Trinitrodibromotoluene (m. p. 229°) is slowly reduced by means of tin and hydrochloric acid; after purification, the resulting *triamidotoluene* is colourless and crystalline; the *hydrochloride*, $C_6H_2Me(NH_2)_3 \cdot 3HCl$, crystallises in various forms, depending on the temperature and concentration of the solution. The *sulphate* and *picrate* are also crystalline, the former being deposited in short prisms. J. B. T.

Composition of the Isodiazohydroxides. By EUGEN BAMBERGER (*Ber.*, 1896, **29**, 1383—1388; compare this vol., i, 246).—The author has succeeded in analysing paranitroisodiazobenzene hydroxide and its sodium and silver salts, as well as *primary potassium isodiazobenzenesulphonate*, $SO_3K \cdot C_6H_4 \cdot N_2 \cdot OH + H_2O$. The latter is a lustrous, crystalline precipitate, and is obtained by adding acetic

acid to the dipotassium salt. The *disilver salt*, which has also been analysed, is a crystalline powder which is decomposed by hot water. The hydroxides of isodiazobenzene and isodiazoparatoluene were found to be too unstable for analysis. The *potassium salt* of the latter forms silver-white, nacreous plates.

Phenyl-a-paranitrophenyl-h-phenylmethylformazyl,



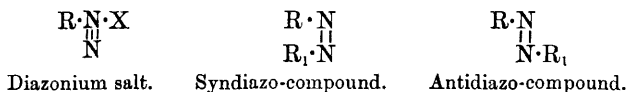
is obtained by the action of paranitroisodiazobenzene hydroxide on benzyldenephnylmethylhydrazine in alcoholic solution at -5° . It crystallises in brownish-red needles, which have a bronze lustre, and melt at $201-202^\circ$; its solution in concentrated sulphuric acid has a deep violet-red colour. This is the first instance of the formation of a formazyl compound by the action of a diazo-compound on a secondary hydrazone.

A. H.

[**Normal Diazo-metallic Salts.**] By EUGEN BAMBERGER (*Ber.*, 1896, **29**, 1388—1390).—The author again maintains the experimental accuracy of his criticism of the results published by Hantzsch (this vol., i, 428).

A. H.

Diazophenols. By ARTHUR R. HANTZSCH and WILLIAM B. DAVIDSON (*Ber.*, 1896, **29**, 1522—1534).—The following arguments are put forward in order to show under which of the three types



the diazophenols and their salts, the salts of paradiazophenolsulphonic acid, and paradiazophenol cyanide should be placed.

The diazophenols behave as the internal anhydrides of very weak bases; they are now found to have a very low electrical conductivity, and, since their cryoscopic behaviour corresponds with a simple molecular weight, this would speak in favour of their being syndiazo-anhydrides; this argument is, however, weakened from the fact that the trimethylamidophenols, which can only be inner ammonium anhydrides, show identical behaviour.

Other considerations, notably the fact that the oxydiazonium ion, $\text{HO} \cdot \text{C}_6\text{H}_4 \cdot \text{N} \equiv \text{N}$, is colourless and insoluble in organic solvents not containing hydroxyl, as are also the anhydrides of the trimethylamidophenols, whilst the ring diazo-compounds are coloured and soluble in organic solvents, points to their being in reality syndiazo-anhydrides, $\text{R} < \overset{\text{N}}{\underset{\text{O}}{\parallel}} \text{N}$. The non-substituted diazophenols appear to

exist in both forms simultaneously, $\text{C}_6\text{H}_4 < \overset{\text{N}}{\underset{\text{O}}{\parallel}} \text{N} \rightleftharpoons \text{C}_6\text{H}_4 < \overset{\text{N} \cdot \text{N}}{\underset{\text{O}}{\parallel}}$.

With regard to the salts of the diazophenols, there can be no doubt as to their being pure oxydiazonium salts. Diazophenol chloride is therefore oxydiazonium chloride, $\text{HO} \cdot \text{C}_6\text{H}_4 \cdot \text{N}_2 \cdot \text{Cl}$. The salts of diazo-

phenolsulphonic acids are, from their stability and their inability to unite with phenols, antidiazo-compounds, $\text{HO}\cdot\text{C}_6\text{H}_4\cdot\overset{\text{N}}{\underset{\text{N}\cdot\text{SO}_3\text{Na}\cdot}{\text{N}}}$. Similarly diazophenol cyanide, $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{CN}$, is stable, and does not combine with phenols; it is therefore probably $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\overset{\text{N}}{\underset{\text{N}\cdot\text{CN}}{\text{N}}}$.

The corresponding acid has been obtained.

Free *paradiazophenol*, $\text{C}_6\text{H}_4\text{N}_2\text{O} + 4\text{H}_2\text{O}$, prepared by the action of moist silver oxide on *paradiazophenol chloride*, forms yellow needles, melting at $38-39^\circ$; it loses water gradually over sulphuric acid, but then decomposes rapidly, especially in the light. Its intensely yellow aqueous solution is only decomposed slowly on boiling; with cadmium iodide, it forms a well-defined crystalline compound, $\text{C}_6\text{H}_4\text{N}_2\text{O} + \text{CdI}_2$.

Free *orthodiazophenol* could not be obtained in the solid state. The *meta*-compound is so unstable that its chloride decomposes in aqueous solutions at 0° .

The following double salts have been isolated.

$\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\text{Cl}\cdot\text{HgCl}_2 + \text{H}_2\text{O}$ [$\text{HO} : \text{NNCl} = 1 : 4$], white needles, decomposing at 156° .

$\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\text{I}\cdot\text{HgI}_2$ [$\text{HO} : \text{NNI} = 1 : 4$] is unstable, and melts at 110° .

$\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\text{I}\cdot\text{HgI}_2 + \text{C}_6\text{H}_4\text{N}_2\text{O}$ is stable, and melts at 132° . The similar compound with cadmium iodide melts at 134° .

Antiparadiazophenol cyanide, $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{N}\cdot\text{N}\cdot\text{CN}$, prepared from *paradiazophenol chloride* and potassium cyanide, forms yellow needles which explode at 117° .

Potassium antidiazophenolcarboxylate, $\text{OK}\cdot\text{C}_6\text{H}_4\cdot\text{N}\cdot\text{N}\cdot\text{COOK}$, is formed from this cyanide by the action of alcoholic potash; it is very unstable.

The authors conclude with a comparison between the diazo- and the trimethylamido-phenols, and finally describe free *diazanthranilic acid*, $\text{C}_6\text{H}_4\cdot\overset{\text{N}:\text{N}}{\underset{\text{CO}_2}{\text{N}}}$, or, more correctly, *diazoniumanthranilic acid*. It is made by diazotising anthranilic acid, and is very unstable, exploding violently when rubbed, whilst its aqueous solution decomposes slowly, with the formation of salicylic acid. J. F. T.

Action of Benzene Sulphonic Chloride on Nitrosodimethylaniline. By ERNST BÖRNSTEIN (*Ber.*, 1896, 29, 1479—1488).—By acting on nitrosodimethylaniline with benzenesulphonic chloride in benzene solution, at ordinary temperatures, the following substances were isolated.

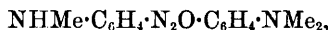
Tetramethylazoxyaniline, $\text{ON}_2(\text{C}_6\text{H}_4\cdot\text{NMe}_2)_2$, is obtained by shaking the benzene solution after the reaction, with dilute sulphuric acid, precipitating the acid solution with sodium carbonate, and washing thoroughly with water; it melts at 244.5° , and forms small, brown crystals.

After the extraction with sulphuric acid, the benzene solution is evaporated to dryness and treated with cold absolute alcohol, when it yields a soluble and an insoluble product.

The latter melts at 183° and crystallises from hot alcohol in yellow plates; it appears to be an azo-peroxide, formed by the condensation of two molecules of nitrosodimethylaniline, and containing the group



The portion soluble in alcohol, on evaporation, yields a brown, crystalline mass, from which, on recrystallisation from methylic alcohol, cinnabar-red crystals of *trimethylazoxyaniline*,



melting at 144° , are obtained; this is interesting from the fact that it is the only asymmetrical azoxy-compound known.

Paranitrosophenylic benzenesulphonate, $\text{Ph}\cdot\text{SO}_3\cdot\text{C}_6\text{H}_4\cdot\text{NO}$, is also found in the benzene solution after treatment with sulphuric acid; it melts at 132° , and forms long, light yellow prisms from dilute alcohol.

J. F. T.

Reduction by means of Phenylhydrazine. By REINHOLD WALTHER (*J. pr. Chem.*, 1896, [2], 53, 433—471; compare Abstr., 1895, i, 595).—Details of the processes requisite for the reduction of nitrobenzene to aniline, of nitrotoluenes to the corresponding toluidines, of metadinitrobenzene to metanitriline, of ortho-nitriline to orthophenylenediamine, of orthonitrophenol to orthamidophenol, of paranitrophenol to paramidophenol, and of orthonitrobenzoic acid to orthamidobenzoic acid, by means of phenylhydrazine are given; except in the last three cases, the nitro-compound is heated with three molecular proportions of phenylhydrazine at first at atmospheric pressure and finally in an autoclave, xylene being used as a diluent when the action is violent. The acid character of the nitrophenols and of the nitrobenzoic acid entails the use of a larger proportion of phenylhydrazine than that given above. The action of phenylhydrazine on azoxybenzene, and on phenylhydroxylamine is very energetic, aniline being among the products. Nitromethane and nitroethane are attacked with difficulty by phenylhydrazine; ethylic nitrate reacts explosively. For the behaviour of phenylhydrazine towards nitroso-compounds consult O. Fischer and Wacker (Abstr., 1888, 1286; 1889, 702) whose work is here confirmed. Bamberger's diazohydroxyamidobenzene (this vol., i, 222) was obtained from nitrosobenzene and phenylhydrazine.

Attempts to obtain symmetrical phenylmethylhydrazine by the reduction of formylphenylhydrazine by phenylhydrazine failed. Neither the group $\text{C}\cdot\text{N}$, as it occurs in the hydrazones, nor the group $\text{C}\cdot\text{C}$ can be reduced by phenylhydrazine.

The nitrobenzylidenephenyldrazones have been prepared by Pickel (Abstr., 1886, 545) and by Lepetit (Abstr., 1887, 845). The *benzoyl*- and *acetyl* derivatives of the meta-compound are colourless, and melt at 197° and 170° respectively; the *benzoyl* and *acetyl* derivatives of the para-compound are also colourless and melt at 169° and 160 — 162° respectively; *benzoylorthonitrobenzylidenephenyldiazone* crystallises in yellow prisms, and melts at 166 — 167° . The nitro-compounds

are readily reduced by phenylhydrazine when heated therewith under pressure; *metamidobenzylidenephnylhydrazone* crystallises in light yellow needles and melts at 162° ; the *para*-derivative in golden-yellow laminae, melting at 175° ; and the *ortho*-derivative in greenish-yellow laminae, melting at $221\text{--}222^{\circ}$.

The foregoing benzoyl and acetyl derivatives were conveniently prepared by treatment of the hydrazone with the acid chloride in a pyridine solution and subsequent addition of water. The same method served for the preparation of benzoylbenzylidenephnylhydrazone which was found to melt at 114° (compare Abstr., 1887, 820).

Azobenzene was readily reduced to hydrazobenzene when heated with phenylhydrazine and the product was free from the camphor odour usually ascribed to it; by the further action of phenylhydrazine, aniline and benzene were formed. Amidoazobenzene is similarly reduced to paraphenylenediamine, aniline, benzene, and nitrogen. Diazoamidobenzene (best purified by recrystallisation from alcohol, not from light petroleum as commonly stated) yielded aniline, benzene, and nitrogen. By heating thiocarbanilide and phenylhydrazine in alcohol, diphenylthiosemicarbazide may be obtained; this undergoes a further change, not yet defined, when heated under pressure with phenylhydrazine. The behaviour of amidines with phenylhydrazine is briefly described and it is pointed out that phenylhydrazine undergoes self reduction to aniline, benzene, nitrogen, and ammonia when heated in an autoclave at 300° .

A. G. B.

Action of Formaldehyde on Phenylhydrazine in Acid Solution.

By CARL GOLDSCHMIDT (*Ber.*, 1896, 29, 1361—1362).—The compound $\text{CH}_2(\text{NPh}\cdot\text{N}\cdot\text{CH}_2)_2$ is formed by the action of phenylhydrazine hydrochloride and methylenedimethyl ether in presence of hydrochloric acid at the ordinary temperature; it is deposited in pale yellow crystals, and melts at 112° ; the molecular weight was determined by the cryoscopic method. The presence of phenylhydrazine in excess favours the formation of the compound, but it could not always be successfully prepared. When gently heated with phenylhydrazine in presence of hydrochloric acid, formaldehyde yields a compound which possibly has the formula $\text{CH}_2\langle\text{NPh}\cdot\text{NMe}\rangle\text{CO}$; it crystallises in rhombic plates, melts at 128° , and gives a reddish-violet coloration with ferric chloride and hydrochloric acid. It is completely decomposed by heating with concentrated hydrochloric acid. The *hydrochloride*, formed in ethereal solution, is unstable.

J. B. T.

Action of Formaldehyde on *as*-Phenylmethylhydrazine in Acid Solution. By CARL GOLDSCHMIDT (*Ber.*, 1896, 29, 1473).—Unsymmetrical phenylmethylhydrazine in hydrochloric acid solution gives a green colour with formaldehyde when allowed to remain for half an hour, or at once on warming in the water bath. No other aldehydes give this reaction, which may, therefore, be used as a test for formaldehyde. From the greenish, creamy mixture, ether extracts a yellowish-white substance melting at 217° , possibly with the constitution $\text{CH}_2(\text{C}_6\text{H}_4\cdot\text{NMe}\cdot\text{N}\cdot\text{CH}_2)_2$. This colours silk and wool bluish.

green; from its alcoholic solution sodium hydroxide precipitates the colour-base as a yellowish-brown substance. C. F. B.

Symmetrical Carbamides of the Benzene Series. By PAUL CAZENEUVE and MOREAU (*Compt. rend.*, 1896, 122, 1130—1131).—When boiled with aniline, guaiacol carbonate readily yields symmetrical diphenylcarbamide, identical with that obtained by the action of carbonyl chloride on aniline. It crystallises in needles which melt at 234—235°, and sublimes at 245°; it is only slightly soluble in cold alcohol and ether, more soluble in boiling alcohol, insoluble in chloroform and benzene. Previous descriptions of the physical properties of this compound seem to be incorrect.

Diparatolylcarbamide, obtained in a similar manner from paratoluidine, forms white crystals which melt at 244—245° and volatilise at the same temperature without decomposing. It is insoluble in most solvents, but can be crystallised from boiling alcohol.

Diorthotolylcarbamide separates from boiling alcohol in magnificent, white, silky crystals, which melt and sublime at 219—220°. It is very slightly soluble in most solvents.

All these substituted carbamides dissolve in concentrated sulphuric acid, and are precipitated unchanged on addition of water. If, however, they are heated with the acid above 115°, they are converted into sulphonic acids, with evolution of carbonic anhydride.

C. H. B.

Halogen Derivatives of Fatty Amines. By A. LUCHMANN (*Ber.*, 1896, 29, 1420—1433).—*Ethyl α-phenoxybutyrate*,



the product of the action of sodium phenoxide on ethyl α-bromobutyrate at 125—130°, distils at 250—251° at 748 mm. pressure; sp. gr. = 1.0388 at 24.5°; it has a faintly aromatic odour, and is insoluble in water, but miscible with alcohol and ether. *α-Phenoxybutyric acid*, $\text{OPh}\cdot\text{Et}\cdot\text{CH}\cdot\text{COOH}$, is somewhat soluble in hot water, but not in cold, dissolves readily in alcohol and ether, but is only sparingly soluble in petroleum; it forms long odourless, colourless, shining needles, melts at 96—99°, and cannot be distilled without decomposing, but may be volatilised in steam; at 180° it is decomposed with liberation of phenol. The *silver salt*, $\text{C}_{10}\text{H}_{11}\text{O}_3\text{Ag}$, melts and decomposes at 202°; the *chloride* is instantaneously decomposed by water, and cannot be distilled without decomposing even under very low pressure (20 mm.). The *amide* dissolves readily in the ordinary media, crystallises in long needles, melts at 111°, and is slightly volatile even at 100°.

α-Phenoxybutyronitrile, $\text{OPh}\cdot\text{CHEt}\cdot\text{CN}$, is obtained in satisfactory amount when the amide is distilled with phosphorus pentachloride; it forms a colourless oil, insoluble in water, and boiling at 228—230° under 148 mm. pressure; unlike phenoxyacetonitrile, it is not reduced to an amide when treated in alcoholic solution with metallic sodium, being merely hydrolysed by this treatment. *α-Phenoxybutyrolthiamide*, $\text{OPh}\cdot\text{CHEt}\cdot\text{CSNH}_2$, is soluble in alcohol, but is insoluble both in ether and in cold water; it crystallises from hot water

in beautiful, shining needles, volatilises slightly at 100° , and melts at 127° , and is not reduced by sodium and absolute alcohol.

An attempt to prepare β -phenoxypropionic acid by the interaction of β -iodopropionic acid and sodium phenoxide failed, the product consisting entirely of an unsaturated compound of low boiling point (90 – 100°), probably phenylic acrylate.

β -Ethoxybutyronitrile is readily reduced in alcoholic solution by means of sodium, yielding γ -ethoxybutylamine (Bookmann, this vol., i, 200); its sp. gr. = 0.8468 at 19° .

γ -Ethoxybutylamine and phenylthiocarbimide unite to form γ -ethoxybutylphenylthiocarbimide, $\text{NHPh}\cdot\text{CS}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CHMe}\cdot\text{OEt}$, which crystallises from absolute alcohol in large, colourless needles, melting at 91.5° . γ -Chlorobutylamine is formed when γ -ethoxybutylamine is heated, in sealed tubes, with fuming hydrochloric acid at 150° ; it is only slightly volatile, and has a strong basic odour; the *hydrochloride* forms a brownish hygroscopic mass of crystals; the *platinochloride*, $(\text{C}_4\text{H}_9\text{Cl}\cdot\text{NH}_2)_2\cdot\text{H}_2\text{PtCl}_6$, crystallises from hot water in golden-yellow leaflets, is readily soluble in alcohol, and melts and decomposes at 212° ; the *picrate*, $\text{C}_4\text{H}_9\text{ClNH}_2\cdot\text{C}_6\text{H}_3\text{N}_3\text{O}_7$, is readily soluble in water and alcohol, and crystallises from the former in yellow, rhombic tables; it melts at 144 – 146.5° , and at 200° decomposes, evolving gases. The *benzoyl* derivative forms an oil which solidifies in a freezing mixture, and is decomposed by alkali at 100° , yielding an oil volatile in steam, which appears to be 2 : 4-*phenylmethylpentoxazoline*, $\text{N}\langle\begin{smallmatrix} \text{CPh} & \text{O} \\ \text{CH}_2 & \text{CH}_2 \end{smallmatrix}\rangle\text{CHMe}$. The latter dissolves somewhat readily in alcohol, water, and ether, and has the characteristic odour of the oxazolines. Its *picrate*, $\text{C}_{11}\text{H}_{13}\text{ON}\cdot\text{C}_6\text{H}_3\text{N}_3\text{O}_7$, forms slender, yellow needles, is sparingly soluble in water and alcohol, sinters at 141° , and melts at 146 – 148° ; at 220° it begins to decompose. γ -Chlorobutylamine and carbon bisulphide unite in presence of alkali, and yield 4-*methylpentthiazoline 2-hydrosulphide*, $\text{N}\langle\begin{smallmatrix} \text{C}(\text{SH})\cdot\text{S} \\ \text{CH}_2 & \text{CH}_2 \end{smallmatrix}\rangle\text{CHMe}$; this crystallises from hot water in beautiful, long, feathery needles, dissolves readily in alcohol, chloroform, benzene, and alkalis, sparingly in ether and hot water, and is insoluble in acids; it sinters at 128° , and melts at 131° . The *ethosulphide*, $\text{C}_4\text{H}_9\text{NS}\cdot\text{SEt}$, is a clear, colourless liquid with a disagreeable odour of mercaptan, which boils at 256° under 754 mm. pressure, and dissolves readily in acids; its *platinochloride*, $(\text{C}_4\text{H}_9\text{NS})_2\cdot\text{H}_2\text{PtCl}_6$, crystallises from warm water in four-sided rhombic tables, and melts and decomposes at 151° ; the *picrate* and the *dichromate* are oils, and do not solidify when cooled.

n-Phenylbutylene- γ -thiocarbimide, $\text{CH}_2\langle\begin{smallmatrix} \text{CHMe}\cdot\text{S} \\ \text{CH}_2 & \text{NH} \end{smallmatrix}\rangle\text{C:NPh}$ or $\text{CH}_2\langle\begin{smallmatrix} \text{CHMe}\cdot\text{S} \\ \text{CH}_2 & \text{N} \end{smallmatrix}\rangle\text{C:NHPh}$, is the product of the interaction of phenylthiocarbimide and γ -chlorobutylamine in presence of alkali. It crystallises from dilute alcohol in long needles, softens at 104° , melts at 106.5° , and dissolves in alcohol, ether, and acids, but is insoluble in water; the *picrate*, $\text{C}_{11}\text{H}_{14}\text{NS}\cdot\text{C}_6\text{H}_3\text{N}_3\text{O}_7$, crystallises from hot

water in yellow needles, melts at 158—164°, and decomposes at 230°. γ -Chlorobutylamine and allylthiocarbimide yield *n*-allylbutylene- ψ -thiocarbamide, $C_8H_{14}N_2S$; this forms an oil which does not solidify at low temperatures; the *picrate*, $C_8H_{14}N_2S \cdot C_6H_3N_3O_7$, crystallises from hot water in long needles, softens at 119° and melts at 121—122°, commencing to decompose at about 220°.

Isocrotylamine ($CH_2 \cdot CH \cdot CH_2 \cdot CH_2 \cdot NH_2$?) is produced when dilute alcoholic potash acts on γ -chlorobutylamine during five hours at 180°. The free base is very volatile, fumes in the air, and has a powerful odour reminiscent of allylamine; it boils at 80—90°. The *hydrochloride* unites with bromine, and appears to yield γ -chlorobutylamine when its solution is evaporated in presence of free hydrochloric acid. The *platinochloride*, $(C_4H_7 \cdot NH_2)_2 \cdot H_2PtCl_6$, dissolves readily in hot water, less readily in cold water and alcohol; it crystallises from saturated alcoholic solutions in well-formed, golden-yellow, six-sided tables or prisms, which melt at 204°. The action of phenylthiocarbimide on the free base affords *phenylisocrotyl*(²)*thiocarbamide*, $NHPh \cdot CS \cdot NH \cdot C_4H_7$; this crystallises from dilute alcohol in slender needles, which melt at 94—97°. The properties of the foregoing compounds are not sufficiently distinct from those of derivatives of crotylamine (compare Schindler, *Abstr.*, 1892, 32) to establish their non-identity with the latter; it is probable, however, that Schindler's base is identical with that obtained by Bookmann (*loc. cit.*) from β -chlorobutylamine.

A. L.

Benzimidoethyl and Benzimidomethyl Ethers. By FRANK W. BUSHONG (*Amer. Chem. J.*, 1896, 18, 490—491).—*Benzimidoethyl ether*, $C_6H_5 \cdot C(NH) \cdot OEt$, was prepared by passing dry hydrogen chloride into benzonitrile and alcohol; the crystalline hydrogen chloride additive product was decomposed by caustic soda, and the new ether extracted by ether; it boils at 218°. *Benzimidomethyl ether* (*Abstr.*, 1895, i, 522) was analogously prepared; it boils at 206°. Both ethers are colourless, mobile liquids with a pleasant odour; neither is solid at -30° .

A. G. B.

Action of Benzaldehyde on Diethyl Ketone. By DANIEL VORLÄNDER and KARL HOBOHM (*Ber.*, 1896, 29, 1352—1353; compare *Abstr.*, 1894, i, 527).—Benzaldehyde (2 mols.) and diethyl ketone (1 mol.) combine in presence of alcohol and alkali, forming *diphenyldimethyltetrahydro- γ -pyrone*, $CO < \begin{smallmatrix} CHMe \cdot CHPh \\ CHMe \cdot CHPh \end{smallmatrix} > O$; it is also obtained in small quantity during the preparation of benzylidene-diethyl ketone. It is crystalline, melts at 106°, boils at 235—237° (20 mm.), and slowly solidifies. Acetic anhydride is without action on the compound. The *dibromo-derivative*, $CO < \begin{smallmatrix} CBrMe \cdot CHPh \\ CBrMe \cdot CHPh \end{smallmatrix} > O$, or $CO < \begin{smallmatrix} CHMe \cdot CBrPh \\ CHMe \cdot CBrPh \end{smallmatrix} > O$, crystallises in lustrous, white plates, melting and decomposing at 144°. Diethyl ketone differs from acetone in its behaviour towards benzaldehyde, since Claisen readily obtained dibenzylideneacetone. The formation of the pyrone is probably preceded by that of the ketoglycol $CO(CHMe \cdot CPh \cdot OH)_2$.

J. B. T.

Diacetylmesitylene. By VICTOR MEYER (*Ber.*, 1896, **29**, 1413—1414).—When mesitylene and acetic chloride, dissolved in carbon bisulphide, are warmed in presence of aluminium chloride, diacetylmesitylene is formed; it is also produced when acetylmesitylene is treated in a similar manner. It crystallises from light petroleum in white prisms, melts at 46° , and boils at 310° (corr.).

So far only durene, isodurene, and mesitylene have afforded diacetyl derivatives by this reaction, in all these substances, the acetyl group must of necessity assume the ortho-position with regard to two methyl groups.

Diacetylmesitylene, although it is a methylated 1 : 5-diketone, does not appear to undergo the characteristic condensation of this class of compounds, namely, the production of a six-carbon ring with elimination of water. This fact is of interest as evincing the greater rigidity of the benzene nucleus as compared with those of aliphatic compounds. A. L.

Chemistry of Etherification. By VICTOR MEYER (*Ber.*, 1896, **29**, 1397—1402).—(I) The author, in conjunction with C. SOHN, has obtained a small amount of prehnitic acid, by the hydrolysis of the ethereal salt formed by the action of alcoholic hydrogen chloride on crude mesitylenic acid prepared from acetone. This appears to confirm the observations of Lucas, from which he concluded that mesitylene from acetone contains hemellitene (this vol., i, 418).

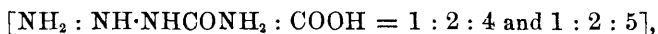
(II) *sym*-Trinitrobenzoic acid, which is not etherified by the action of alcoholic hydrogen chloride, even after treatment for 30 days, is readily converted into the methylic salt when its silver salt is heated with methylic iodide. Cetylic iodide also acts quite readily on the silver salt, producing the *cetylic* salt, which forms white crystals melting at 121 — 122° . It can be distilled in small quantities without undergoing decomposition. 1 : 2-Hydroxynaphthoic acid behaves in a similar manner. It appears, therefore, that the molecular volume of the alkyl radicle to be introduced by the action of the iodide on the silver salt does not affect the reaction.

(III) The best method to employ in order to ascertain whether an acid can be etherified or not by means of alcoholic hydrogen chloride is that originally proposed by E. Fischer, which consists in boiling the acid for three to five hours with alcohol containing 3 per cent. of hydrogen chloride.

(IV) Hemimellitic acid, $C_6H_3(COOH)_3$ [1 : 2 : 3], only yields a dimethylic ether in the cold, when it is treated with hydrogen chloride dissolved in methylic alcohol. When the reaction is carried out at a higher temperature, a small amount of the trimethylic salt is formed, its production being probably due to the preliminary formation of a certain amount of anhydride at the temperature of the experiment. A. H.

Azimido Compounds. IV. Azimidouramidobenzoic acids and Azimidobenzoic acids. By THEODOR ZINCKE and BRUNO HELMERT (*Annalen*, 1896, **291**, 313—342; compare this vol., i, 300).

—The object of the investigation has been already explained (*loc. cit.*); and the result at which the authors have arrived is to the effect that the azimidouramidobenzoic acids obtained by the action of nitrous acid on the amidouramidobenzoic acids,



are most probably not identical; it is more likely that they are two different acids which give rise to the same azimidobenzoic acid.

Metauramidobenzoic acid (Menschutkin, *Annalen*, 1870, **153**, 84), $\text{COOH} \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{CO} \cdot \text{NH}_2$, crystallises from hot alcohol in aggregates of leaflets, and melts and decomposes at 269—270°; the *methylic* salt crystallises from glacial acetic acid in needles, and melts at 185°.

Metauramidodibenzoic acid, $\text{CO}(\text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{COOH})_2$, Griess' carbodibenzamic acid, is obtained by boiling an aqueous solution of barium *m*-uramidobenzoate; it is insoluble in common agents, and does not melt below 270°. Contrary to the statement of Sarauw (*Abstr.*, 1882, 608) the ammonium salt is capable of existence in aqueous solution if excess of ammonia is present; the *methylic* salt crystallises from methylic alcohol in lustrous leaflets, and melts and decomposes at 223°.

4:3-Nitrouramidobenzoic acid is prepared by nitrating uramidobenzoic acid, and treating the mixture of dinitro-acids thus obtained with boiling ammonia; it is almost insoluble in ether and acetone, and crystallises from water in slender, yellow needles, which become red and decompose at 220°. The *ammonium* salt crystallises in lustrous, golden-yellow needles, and the *barium* salt, which dissolves sparingly in water, separates in small, yellow needles; the *methylic* salt crystallises from methylic alcohol in sulphur-yellow needles, and melts at 184°. The action of boiling water or boiling dilute acetic acid, during a protracted period, converts the acid into 4:3-nitramidobenzoic acid.

4:3-Amidouramidobenzoic acid is obtained by reducing nitrouramidobenzoic acid with tin and hydrochloric acid; it crystallises from water in small, slender needles, and does not melt below 270°. The *barium* salt dissolves somewhat readily in water, and crystallises in white needles; the silver salt rapidly darkens in light, and deposits silver when the solution in glacial acetic acid is boiled.

3:4-Amidocarboxamidobenzoic acid, $\text{COOH} \cdot \text{C}_6\text{H}_3 < \begin{smallmatrix} \text{NH} \\ \text{NH} \end{smallmatrix} > \text{CO}$, is produced when the foregoing acid is treated with boiling water or boiling dilute hydrochloric acid (compare Griess, this Journal, 1872, 497); it is insoluble in common agents, and does not melt below 270°. The *ammonium* salt crystallises in white needles, and decomposes in absence of excess of ammonia; the barium and silver salts are amorphous, and the *methylic* salt separates from glacial acetic acid in the form of a fine powder.

Azimidometauramidobenzoic acid, $\text{COOH} \cdot \text{C}_6\text{H}_3 < \text{N}(\text{CONH}_2) \text{N} >$, has not been obtained in the pure state; the authors, however, regard it as distinct from the para-compound, and consequently represent its

constitution by the foregoing expression. It is obtained by dissolving 4 : 3-amidouramidobenzoic acid in the minimum quantity of hot water, adding sodium nitrite to the cold solution, and then acidifying with hydrochloric acid; it is a white, amorphous powder, dissolving with great difficulty in ordinary organic solvents, excepting glacial acetic acid, and may be heated to 270° without undergoing fusion. On dissolving the acid in alkalis, it undergoes hydrolysis, yielding azimidobenzoic acid, carbonic anhydride, and ammonia; the same change is effected by boiling solvents.

Parauramidobenzoic acid is obtained from paramidobenzoic acid and potassium cyanate by the method adopted in preparing the meta-acid; although Griess (this Journal, 1872, 711) did not succeed in obtaining it crystalline, the acid separates as a white, crystalline powder, and does not melt below 270° . The *ammonium* salt crystallises in monoclinic plates, the *barium* and *silver* salts are amorphous, and the *methylic* salt crystallises from alcohol, and melts at 252° .

Parauramidodibenzoic acid arises from the foregoing acid when a solution of the barium salt is boiled during a protracted period; it is an amorphous substance, dissolving with great difficulty in common agents, and does not melt below 270° . The *ammonium* salt crystallises in lustrous leaflets, the *calcium*, *barium*, and *silver* salts are amorphous, and the *methylic* salt crystallises from methyl alcohol in small, white plates, which melt, evolving gas, at 246° .

Dinitroparauramidobenzoic acid is obtained by the action of fuming nitric acid on *p*-uramidobenzoic acid; it dissolves with difficulty in organic agents, becomes dark yellow at 190° , and melts at $268-270^{\circ}$. When treated with hot alkali, it yields 3 : 4-nitramidobenzoic acid. The *ammonium* salt is readily soluble in water.

3 : 4-Nitrouramidobenzoic acid is produced when the foregoing acid is treated with boiling ammonia, nitrous oxide being liberated; it crystallises from 50 per cent. acetic acid in small, yellow needles, and melts and decomposes at 221° . The *ammonium* salt dissolves readily in water, and the *barium* salt, which contains $3H_2O$, crystallises from water in slender, yellow needles; the *methylic* salt crystallises from methyl alcohol in small, yellow needles, and melts at 189° .

3 : 4-Amidouramidobenzoic acid crystallises from hot water in small, white needles, and does not melt below 270° ; it is sparingly soluble in organic agents, and quickly reduces platinum tetrachloride. When the aqueous solution is boiled, 3 : 4-amidocarboxamidobenzoic acid (see above) is produced, the change being accelerated by the influence of hydrochloric acid. The *ammonium* salt crystallises in slender, white needles, and the *barium* salt, which dissolves readily in alcohol, also forms white needles; the *silver* salt is amorphous, and darkens rapidly when heated.

Azimidoparauramidobenzoic acid, $COOH \cdot C_6H_3 < \overline{N(CONH_2)}^N > N$, is produced when 3 : 4-amidouramidobenzoic acid is treated with nitrous acid; it crystallises from a large volume of absolute alcohol in small needles, and does not melt below 270° . Treatment with boiling water, alcohol, or glacial acetic acid converts it into azimidobenzoic acid, and the same effect is produced by dissolution in cold alkalis.

3:4-Azimidobenzoic acid, $N \begin{smallmatrix} \nwarrow NH \\ \nearrow N \end{smallmatrix} > C_6H_4 \cdot COOH$ [COOH : N : NH = 1 : 4 : 3 or 1 : 3 : 4], is produced by the action of sodium nitrite on an aqueous solution of orthodiamidobenzoic acid hydrochloride, and crystallises from water in small needles, and from glacial acetic acid in lustrous leaflets, which do not melt below 270°. The sodium salt separates from methylic alcohol in crystals containing the solvent, and the barium salt contains 4H₂O; the silver salt dissolves in ammonia, and the methylic salt crystallises from methylic alcohol in rhombic plates, and melts at 170—171°. Azimidobenzoic acid also yields a hydrochloride, which dissolves very readily in water, and loses hydrogen chloride over sulphuric acid.

The chloride of dimethylazammoniumbenzoic acid,



crystallises in slender, white needles, and melts and decomposes at 238°; the platinochloride crystallises in orange-yellow cubes and leaflets.

Methylazimidobenzoic acid, $COOH \cdot C_6H_3 \cdot N_3Me$, is obtained by eliminating methylic chloride from the foregoing chloride; it crystallises from water in aggregates of very small needles, and melts above 270°.

The betaine of dimethylazammoniumbenzoic acid, $C_6H_3 \begin{smallmatrix} \nwarrow COO \\ \nearrow N_3Me_2 \end{smallmatrix}$, is obtained by heating azimidobenzoic acid with methylic alcohol and the iodide, treating the liquid with water, and agitating with freshly prepared silver oxide; it crystallises from absolute alcohol in slender needles, and melts at 247°.

Acetazimidobenzoic acid, $COOH \cdot C_6H_3 \cdot N_3Ac$, crystallises from alcohol in small needles, and melts and decomposes at 232°.

Both meta- and para-azimidouramidobenzoic acids yield azimidobenzoic acid when dissolved in ammonia, and the solution acidified after remaining for some time; carbonic anhydride is eliminated, and the acid thus obtained is identical in every respect with the substance obtained from 3:4-diamidobenzoic acid.

By oxidising azimidotoluene with potassium permanganate, Bladin (Abstr., 1893, i, 375) obtained 1:2:3-triazoledicarboxylic acid, $N \begin{smallmatrix} \nwarrow N-C \cdot COOH \\ \nearrow NH-C \cdot COOH \end{smallmatrix}$. The same substance, which the authors call azimidoethylenedicarboxylic acid, or osotriazonedicarboxylic acid, is produced by dissolving azimidobenzoic acid in caustic soda, and oxidising it with a 10 per cent. solution of potassium permanganate.

M. O. F.

Hydrated Sodium Salicylate. By GYSBERT ROMYN (*Ned. Tydschr. Pharm., &c.*, 1896, 111—113).—Sodium salicylate, when dissolved in its own weight of water, after a time deposits large prismatic crystals showing double refraction, and containing 6H₂O. If crystallisation will not readily set in, it may be promoted by introducing a crystal from a previous experiment.

As might be expected, the crystals very rapidly effloresce, and the water is quickly expelled on drying at 80°.

L. DE K.

Action of Ethyloxalic Chloride [Ethylic Chloroglyoxylate] on Hydrocarbons of the Benzene Series in presence of Aluminium Chloride. By LOUIS BOUVEAULT (*Compt. rend.*, 1896, **122**, 1062—1064.).—The action of ethylic chloroglyoxylate on benzene hydrocarbons in presence of aluminium chloride and carbon bisulphide yields a considerable quantity of the substituted glyoxylic salts, $R\cdot CO\cdot COOEt$. These are colourless liquids, with a disagreeable odour, and are very stable. Alcoholic potash converts them into resinous products, but aqueous soda gives an excellent yield of the corresponding sodium salts, from which the acids are readily obtained. The acids are crystallisable compounds only slightly soluble in water; they distil without change in a vacuum, but decompose when distilled in presence of air, as Claisen has shown, the products being carbonic oxide and anhydride and a mixture of aldehyde and acid.

The reaction of ethylic chloroglyoxalate on the benzene hydrocarbons is as general as that of the other acid chlorides, and can be extended to the mixed ethers of the aliphatic and benzene series, but not to the phenols nor their acid ethereal salts. As a general rule, when isomerides can be formed, the para-derivative is the chief product, if its formation is possible.

C. H. B.

Reduction of the Benzylaminecarboxylic [exo-Amidotoluic] acids. By ALFRED EINHORN (*Ber.*, 1896, **29**, 1590—1594.).—The substituted *exo*-amidotoluic acids are converted by reduction with amylic alcohol and sodium into two isomeric hexahydro-compounds, which are probably the *cis*- and *trans*-forms of the acid. The *cis*-compounds have probably a betaine-like structure, and are not extracted from solution in amylic alcohol by dilute alkalis, so that the two can be separated in this manner.

The *cis*-acids are all basic oils with a stupefying odour, whilst the *trans*-acids are crystalline.

cis-*exo*-Amidohexahydro-*paratoluic acid* forms a *hydrochloride* which crystallises in long, thin needles melting at 235° . The *platinochloride* melts at 208 — 209° , and the *aurochloride* at 215 — 217° .

exo-Diethylamido-*orthotoluic acid*, $NEt_2\cdot CH_2\cdot C_6H_4\cdot COOH$, is prepared from diethylamine and orthochloromethylbenzamide. It melts at 105° , and yields a *platinochloride* melting at 200° , an *aurochloride* melting at 202° , and a *picrate* melting at 128° .

cis-*exo*-Diethylamidohexahydro-*orthotoluic acid* is an oil; the *hydrochloride* melts at 236 — 238° , the *aurochloride* at 190° , and the *platinochloride* at 198° . *trans*-*exo*-Diethylamidohexahydro-*orthotoluic acid* crystallises in long, slender needles melting at 97° , and is odourless. The *aurochloride* melts at 115° , and the *picrate* at 135° . These acids are accompanied by *exo*-hydroxy-*orthotoluic acid*, $COOH\cdot C_6H_{10}\cdot CH_2\cdot OH$, which melts at $113\cdot 5^{\circ}$.

exo-Diethylamidoparatoluic acid may be prepared from *exo*-chloroparatoluic acid and diethylamine. It forms crystals resembling those of sal ammoniac, and melts at 150° . The *hydrochloride* crystallises with $2H_2O$ in prisms and melts at 185° . The *aurochloride* melts at 156° , the *platinochloride* at 202 — 208° , and the *picrate* at 174 — 176° .

exo-cis-Diethylamidohexahydroparatoluic acid boils at 275—280°; the *hydrochloride* melts at 166—167°. The *hydrochloride* of the *trans-acid* melts at 195°, the *aurochloride* at 162—163°, and the *picrate* at 163—164°.

The *hydrochloride* of *hexahydrophenylamidoacetic acid* crystallises with 2 mols. of alcohol in needles, and melts at 232°. A. H.

Isomerism of Ethylic Formylphenylacetate. By WILHELM WISLICENUS (*Annalen*, 1896, 291, 147—216; compare *Abstr.*, 1895, i, 366; this vol., i, 369; and Claisen, this vol., i, 557).—The author emphasises his opinion that the two forms of ethylic formylphenylacetate are structurally isomeric in the sense already indicated (*loc. cit.*); throughout the description of his investigation, the α -salt refers to the liquid isomeride, which develops coloration with ferric chloride, and is regarded as having the constitution $\text{OH}\cdot\text{CH}\cdot\text{CPh}\cdot\text{COOEt}$, whilst the solid isomeride, which is indifferent towards ferric chloride, and has the constitution $\text{CHO}\cdot\text{CHPh}\cdot\text{COOEt}$, is distinguished as the β -salt. A mixture of both isomerides is obtained by the action of sodium wire on ethylic phenylacetate and ethylic formate in dry ether; on extracting the liquid with water, and rendering acid the extract with sulphuric acid, a partially crystalline mass is obtained, from which the liquid isomeride may be removed by suction. Another method of purifying the crude product consists in adding aqueous copper acetate to the alcoholic solution, and decomposing with acid the copper derivative so obtained.

The α -salt, *ethylic hydroxymethylenepherylacetate* (*ethylic phenylhydroxyacrylate*), $\text{OH}\cdot\text{CH}\cdot\text{CPh}\cdot\text{COOEt}$, boils at 135° and 145° under pressures of 15 mm. and 25 mm. respectively; a specimen containing no crystals of the solid modification, or one which has been heated at 70—80° during one hour, may be preserved indefinitely without undergoing molecular rearrangement, whilst the presence of the solid form induces conversion into this isomeride. The sp. gr. = 1.12435 at 15°/15°, and 1.12045 at 20°/20°.

The β -salt, *ethylic formylphenylacetate*, $\text{CHO}\cdot\text{CHPh}\cdot\text{COOEt}$, is purified by treating the crystals first obtained with chloroform or benzene, and finally with ether, until indifference towards ferric chloride indicates the complete removal of the α -modification. The melting point is approximately 70°, but is somewhat indefinite, owing to the production of a certain amount of the isomeride when the solid is heated. The pure salt may be preserved unchanged in closed tubes, and does not, as previously stated, undergo transformation into the isomeride unless subjected to the influence of moisture or the vapour of solvents. Determinations of the molecular weight, as in the case of the liquid form, are in agreement with the formula $\text{C}_{11}\text{H}_{12}\text{O}_2$; the sp. gr. = 1.271. The heat of combustion of the α -salt at constant volume is 1318.7 Cals. per gram-molecule, and 1319.8 Cals. under constant pressure; the corresponding values for the β -modification are 1315.5 Cals. and 1316.4 Cals. respectively.

The striking difference in behaviour towards ferric chloride exhibited by the two forms, has enabled the author to investigate systematically the influence of solvents on the transformation of one

into the other. When either modification is dissolved in alcohol, the solution very soon contains both forms, until, after two days, a condition of equilibrium is reached, and the liquid, whether obtained originally from the α - or the β -salt, exhibits the same intensity of coloration with ferric chloride. Other solvents, however, do not yield a solution containing equal quantities of the two salts, the proportion of each existing in the liquid when the condition of equilibrium is attained, depending entirely on the nature of the medium, and the temperature and concentration of the solution; thus methylic alcohol, a solvent of high dissociating power, is favourable to the existence of the β -salt, whilst solutions in chloroform and benzene contain only the α -modification, the influence of high temperature and an increased degree of concentration being in the same direction. The results of a spectrochemical investigation, carried out by Brühl, establish the formula already ascribed to the α -salt, and indicate that an alcoholic solution of the β -salt contains, in reality, both modifications; the specific magnetic rotatory power of the α -salt is 2.0369 at 15° , and of the β -salt, dissolved in benzylic alcohol, 2.1047 at 17.5° ; the experiments carried out by Perkin leading to the same conclusion as those on the molecular refraction. Traube's determinations of the molecular solution volumes establish the constitution of the α -salt, and yield results which are not in agreement with the aldehydic formula for the β -modification; an explanation of the latter fact is probably to be found in the existence of one-third or a half of the β -salt in the form of complex molecules when dissolved.

The *acetate* of ethylic hydroxymethylenepherylacetate,



is produced when either salt is heated with acetic anhydride for one hour at 160° ; it is a transparent oil, which boils at 184° under a pressure of 18 mm. The *dibromide*, $\text{OAc}\cdot\text{CHBr}\cdot\text{CPhBr}\cdot\text{COOEt}$, crystallises from dilute alcohol in small, lustrous prisms, and melts at 67° . The *benzoate* of ethylic hydroxymethylenepherylacetate, $\text{OBz}\cdot\text{CH}\cdot\text{CPh}\cdot\text{COOEt}$, is obtained from both salts, and crystallises from alcohol in large, lustrous, rhombohedra melting at 87 – 88° ; the production of one acetate and benzoate from the two modifications is an argument in favour of a structural difference between the original salts.

Phenylic cyanate is advantageously applied in distinguishing between hydroxy-derivatives and ketones or aldehydes, being indifferent towards the latter groups, and uniting with the former to produce ethereal carbanilides. In the present instance, it is found that the β -salt is indifferent towards the agent, whilst on remaining with it in a sealed tube during several months, the α -modification yields the *carbanilido*-derivative of ethylic hydroxymethylenepherylacetate, $\text{NPh}\cdot\text{CO}\cdot\text{O}\cdot\text{CH}\cdot\text{CPh}\cdot\text{COOEt}$; it crystallises from alcohol in microscopic leaflets, and melts at 116° . In an analogous manner, Claisen's hydroxymethylenebenzylic cyanide, obtained by the action of sodium on benzylic cyanide and ethylic formate, yields the *carbanilido*-derivative, $\text{NPh}\cdot\text{CO}\cdot\text{O}\cdot\text{CH}\cdot\text{CPh}\cdot\text{CN}$, which crystallises from alcohol in small needles, and melts at 153 – 154° ; it develops no

coloration with ferric chloride, but when heated above the melting point, phenylic cyanate is eliminated, and the product develops colour with ferric chloride.

A remarkable feature of the isomerism of ethylic formylphenylacetate is to be found in the fact that this isomerism is probably extended to the metallic derivatives; thus two distinct copper derivatives have been isolated, and there are satisfactory indications that the α -sodium salt undergoes conversion into an isomeride which exists only in solution. Although the author does not claim to have established this principle, he regards the evidence brought forward as opposed to Neff's hypothesis (this vol., i, 71) that metallic derivatives of acidic substances do not exist, having the metal directly united with carbon.

The α -sodium derivative of ethylic hydroxymethylenepherylacetate is obtained as a white powder, which melts indefinitely at 120° , on adding sodium wire to an ethereal solution of the liquid ethylic salt; on treating the dry substance with dilute sulphuric acid, the α -ethylic salt is liberated; but, if excess of the acid is added to an aqueous solution which has remained at the ordinary temperature during one minute, the β -ethylic salt separates immediately in crystals. When carbonic anhydride is led into the solution of either ethylic salt in aqueous soda, the α -ethylic salt separates first, a few crystals of the solid modification being formed when the operation has proceeded during a protracted period; dilute sulphuric acid in small portions, and added slowly, effects the same result; but if the agent is added in excess, the precipitate consists exclusively of the solid form. On treating the solid sodium derivative with ferric chloride, a deep bluish-violet mass is produced, which probably consists of the α -ferric derivative, the solution in alcohol being bluish-violet; the aqueous solution of the sodium derivative, however, although rendered bluish-violet by ferric chloride, becomes much less intensely coloured, and no separation of ferric derivative occurs, whilst after a few minutes, the colour disappears, and the β -ethylic salt separates.

The α -copper derivative of ethylic hydroxymethylenepherylacetate, $C_{22}H_{22}O_6Cu$, obtained on adding aqueous copper acetate to an alcoholic solution of the α -ethylic salt, crystallises from hot alcohol in lustrous, green needles containing 2 mols. of ethylic alcohol; it rapidly effloresces in air and at 80° , melting at 171 – 173° . On dissolving the substance in hot alcohol, a small quantity of an insoluble, dark green compound is produced having the composition $C_{13}H_{16}O_4Cu$. The β -copper derivative is obtained on treating an aqueous solution of the sodium derivative with copper sulphate, the solutions being previously cooled with ice; a bright bluish-green precipitate is formed which yields the β -ethylic salt exclusively when decomposed with sulphuric acid. At ordinary temperatures, and in the dry state, this modification becomes spontaneously converted into the α -isomeride, and, although insoluble in alcohol, the hot agent rapidly produces a green solution, from which the α -derivative crystallises on cooling.

M. O. F.

Spectrochemical Investigation of α - and β -Ethylic Formylphenylacetates. By JULIUS W. BRÜHL (*Annalen*, 1896, 291, 217—

225).—The author has determined the molecular refraction and dispersion of the two forms of ethylic formylphenylacetate, described by W. Wislicenus (preceding abstract). His investigation shows that both forms exist in solution, and whilst the liquid α -salt is accurately represented by the formula $\text{OH}\cdot\text{CH}\cdot\text{CPh}\cdot\text{COOEt}$, the constitution of the solid isomeride may be expressed with equal truth by the formula $\text{CHO}\cdot\text{CHPh}\cdot\text{COOEt}$, or by the geometrically isomeric form of the structure ascribed to the α -salt. M. O. F.

Halogen Derivatives of the Sulphonamides. By J. H. KASTLE, B. C. KEISER, and ERNEST BRADLEY (*Amer. Chem. J.*, 1896, **18**, 491—502).—The compounds here described behave like substitution, rather than additive, derivatives of the sulphonamides; for instance, they explode when rapidly heated, the halogen being evolved, and they are decomposed by strong acids with liberation of the halogen and formation of the sulphonamide; in these two respects, they recall the behaviour of nitrogen trichloride. Furthermore, they are oxidising agents by virtue of the fact that they readily part with their halogen, the original sulphonamide being formed; if they were additive compounds, their oxidising power would be equivalent to that of 1 atom of oxygen, whereas it is found to be equivalent to that of 2 atoms, showing that the compounds are substitution compounds. These collateral evidences are necessary, since analysis cannot be depended on to detect the 2 atoms of hydrogen which constitute the difference between the additive and substitution products.

Benzenedichlorosulphonamide, $\text{C}_6\text{H}_5\cdot\text{SO}_2\cdot\text{NCl}_2$, is prepared by passing a rapid current of chlorine through a solution of benzenesulphonamide in the smallest possible quantity of aqueous soda (1:10); the precipitate is purified by being heated with water, when the chlorine derivative melts, and may be thus separated from unchanged sulphonamide; dissolution in alcohol and precipitation by water complete the purification. It forms nacreous laminæ, melts at 70° , and explodes at 218 — 220° . *Paratoluenedichlorosulphonamide* was prepared in a similar manner; it melts at 80° , and explodes at high temperatures. *Parabromobenzenedichlorosulphonamide* is a white, crystalline powder, melting at 106° .

Benzenedibromosulphonamide, prepared by adding bromine to a solution of benzenesulphonamide in aqueous soda, forms dark yellow laminæ, melts at 110° , evolving some bromine, and explodes when heated suddenly; it is readily soluble in alcohol, ether, chloroform, and carbon bisulphide. *Parachlorobenzenedibromosulphonamide* is a yellow, crystalline substance. A. G. B.

Oxidation of Hydroxylamine by Benzenesulphonic Chloride. By OSCAR PILOTY (*Ber.*, 1896, **29**, 1559—1567).—The compounds $(\text{Ph}\cdot\text{SO}_2)_2\text{N}\cdot\text{OH}$, dibenzenesulphonahydroxylamide, and $(\text{Ph}\cdot\text{SO}_2)_3\text{NO}$, tribenzenesulphonahydroxylamide, are already known; the author has prepared the missing member of the series, $\text{Ph}\cdot\text{SO}_2\cdot\text{NH}\cdot\text{OH}$, *benzenesulphonylhydroxylamide* (*benzsulph-hydroxamic acid*), by adding benzenesulphonic chloride to an alcoholic solution of hydroxylamine; it melts at about 126° , and has but very feeble acid properties, not

even liberating carbonic anhydride from hydrogen carbonates; its *potassium* and *sodium* salts were obtained by adding the alkali methoxides to an alcoholic solution of the acid. It yields a *diacetyl* derivative melting at 85° . Ferric chloride, and also bleaching powder or iodine, oxidise it quantitatively to dibenzenesulphonhydroxylamide acid and nitrous acid; fuming nitric acid oxidises it, although not quantitatively, to tribenzenesulphonhydroxylamide. When it is shaken with 40 per cent. aqueous potassium hydroxide, potassium benzenesulphonate separates, and, by acidifying the solution with acetic acid and adding silver nitrate, a precipitate of silver hyponitrite, mixed with acetate, is obtained; in fact, this is probably the best way of preparing silver hyponitrite. It is thus seen that the action of benzenesulphonic chloride on hydroxylamine may be regarded as an oxidation of the latter taking place in two stages; the hydroxylamine is eventually oxidised to hyponitrous acid, whilst the sulphonic chloride is reduced to a sulphinic acid.

Phenylhydroxylamine brings about a similar series of reactions, yielding *benzenesulphonphenylhydroxylamide*, $\text{Ph}\cdot\text{SO}_2\cdot\text{NPh}\cdot\text{OH}$, melting at 121° , and then benzenesulphinic acid and nitrosobenzene, $\text{Ph}\cdot\text{NO}$. Benzylhydroxylamine, however, only yields the intermediate product *benzenesulphonbenzylhydroxylamine*, $\text{Ph}\cdot\text{SO}_2\cdot\text{N}(\text{CH}_2\text{Ph})\cdot\text{OH}$, melting at $92-93^{\circ}$; the action of sodium hydroxide on this yields only benzaldoxime.

The author has also obtained hyponitrous acid in the solid state, and its ammonium salt too (compare Hantzsch, this vol., ii, 520).

C. F. B.

Orthamidobenzophenone. By CARL GRAEBE and F. ULLMANN (*Annalen*, 1896, **291**, 8-16; compare Abstr., 1895, i, 147).—The paper is an expansion of the preliminary note on the preparation of orthamidobenzophenone and synthesis of acridone (*loc. cit.*).

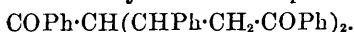
M. O. F.

Condensation of Benzaldehyde with Acetophenone. By STANISLAUS VON KOSTANECKI and G. ROSSBACH (*Ber.*, 1896, **29**, 1488-1494).—When benzaldehyde is condensed with acetophenone in presence of sodium hydroxide, the resulting product depends largely on the conditions of the experiment.

Benzylideneacetophenone, $\text{CHPh}\cdot\text{CH}\cdot\text{COPh}$, is produced when 20 grams of a 10 per cent. solution of sodium hydroxide is added to an alcoholic solution of 21 grams of benzaldehyde and 24 grams of acetophenone, and the reaction allowed to proceed during 24 hours.

Benzylidenediacetophenone, $\text{CHPh}(\text{CH}_2\cdot\text{COPh})_2$, is formed when the reacting substances are in the proportion of 1 mol. of benzaldehyde and 2 mols. of acetophenone. It forms thick prisms, melting at 85° . By distillation, it is decomposed into benzylideneacetophenone and acetophenone.

When 2 mols. of benzaldehyde react with 3 mols. of acetophenone for 24 hours at $40-50^{\circ}$, a substance of the formula $\text{C}_{38}\text{H}_{32}\text{O}_3$, melting at 198° , is produced; if, however, the temperature is raised to 100° , an isomeric substance, melting at 256° , is formed. These are evidently the two stereoisomeric dibenzylidenetriacetophenones,



Dibenzylidenetriacetophenone is a crystalline powder melting at 198° . and very insoluble in alcohol, although easily soluble in acetic acid and warm benzene. When suspended in alcohol and heated on the water-bath, after addition of concentrated sodium hydroxide, it is converted into its isomeride, melting at 256° .

Dibenzylidenetriacetophenone crystallises in glistening plates and melts at 256° ; by distillation, it is decomposed into benzylideneacetophenone and acetophenone. J. F. T.

Action of Alkali on Benzylideneacetophenone and Benzylidenediacetophenone. By STANISLAUS VON KOSTANECKI and JOSEF TAMBOR (*Ber.*, 1896, **29**, 1495—1497; compare preceding abstract).—The two isomeric dibenzylidenetriacetophenones are formed by the condensation of benzylideneacetophenone and acetophenone in the presence of sodium hydroxide, the higher (256°) melting compound being formed at a temperature not higher than 40 — 50° , the lower (198°) at the temperature of the boiling water bath. They are also produced by the action of sodium hydroxide on benzylideneacetophenone without the addition of acetophenone.

In order to show that the dibenzylidenetriacetophenones were additive products of benzylideneacetophenone and benzylidenediacetophenone, and were not formed by the simple rearrangement of the atoms in benzylideneacetophenone, they were made by condensing benzylidenediacetophenone with benzylideneacetophenone in the presence of sodium hydroxide, a very fair yield being obtained. It is, therefore, evident that unsaturated, as well as 1 : 5-diketones, which contain a methylene group next to the carbonyl, are transformed by the action of alkalis into the more stable 1 : 7-triketones.

A good test for the purity of 1 : 5-diketones is the action of concentrated sulphuric acid on them; whereas unsaturated ketones give in this way an orange-yellow colour, the 1 : 5-diketones remain colourless or become slightly yellow (with blue fluorescence), whilst the 1 : 4 : 7-triketones become red. J. F. T.

1 : 3-Diketones. By LUDWIG CLAISEN (*Annalen*, 1896, **291**, 25—137; compare *Abstr.*, 1894, i, 31). I. [With L. FALK].—The paper deals with monobenzoyl derivatives of 1 : 3-diketones, substances which present two possibilities in considering the question of structure. In most cases both isomerides, corresponding with the groups $-C(OH):C \cdot CO-$ and $-CO \cdot CH \cdot CO-$, have been isolated, and are distinguished as the α -, or acidic, and the β -, or neutral modification respectively.

The existence of this isomerism has been contested by Nef, who regards the variation in properties of the two forms as depending on differences of a physical character; in opposition to this view, however, the authors adduce the following facts. (1) Cryoscopic determinations in benzene of the molecular weight of both modifications of dibenzoylacetylmethane yield identical results, and stability of the two forms in this solvent has been already established. (2) The differences in chemical properties exhibited by the isomerides, as, for instance, their behaviour towards ferric chloride and alkali car-

bonates, characterise, not only the solid substances, but also their solutions.

The authors expound their views on the subject of this isomerism, which they regard as structural in character.

The preparation of dibenzoylmethane has been hitherto attended with some difficulty, and a method is described by which the yield may be raised to 80 or 90 per cent. of the theoretical quantity. Improvements have been also effected in the production of benzoylacetylmethane from benzoylacetone, the modification consisting in the employment of an alcoholic solution of the sodium derivative of the diketone, instead of suspending the solid substance in ether; another convenient mode of benzoylating diketones is an application of the process described by Claisen (Abstr., 1895, i, 139), the substance being treated with 1 mol. of benzoic chloride in presence of 2 or 3 mols. of dry sodium carbonate. These methods have been applied successfully in preparing dibenzoylacetylmethane, benzoyldiacetylmethane, ethylic benzoylacetate, and ethylic benzoylmalonate.

α -Dibenzoylacetylmethane, $\text{CBz}_2\text{:CMe}\cdot\text{OH}$ (compare Nef, Abstr., 1894, i, 31), is obtained, in the manner already indicated, from benzoylacetone, benzoic chloride, and sodium carbonate, the triketone being liberated by means of acetic acid; it separates from petroleum in short, colourless prisms, belonging to the monoclinic system; $a:b:c = 1.0271:1:4.8560$, and $\beta = 121^\circ 54'$. It melts almost completely at $80\text{--}85^\circ$, solidifies at $87\text{--}89^\circ$, and melts again at $99\text{--}101^\circ$; these phenomena are exhibited less definitely by an uncrystallised specimen, and as they probably depend on an isomeric change, the authors regarded it as probable that the freshly precipitated substance contains a certain amount of a hydrate yielding the isomeride below the melting point of the α -modification, but this view was negatived by experiment.

β -Dibenzoylacetylmethane, CHAcBz_2 , is obtained by boiling a solution of the α -modification in 50 per cent. alcohol, and allowing the liquid to cool spontaneously; it crystallises in snow-white needles, and melts at $107\text{--}110^\circ$, no indication of initial fusion at $80\text{--}85^\circ$ being observed. The conversion of one modification into the other is not completely effected by absolute alcohol, the α -triketone crystallising for the most part unchanged; the greater the dilution of the solvent, however, the more complete is the transformation. Careful cryoscopic determinations have established the identity of the molecular weight of the two forms; the experiments were conducted in benzene, it having been previously shown that no molecular rearrangement occurs in this medium. Whilst α -dibenzoylacetylmethane develops a red coloration with ferric chloride, and exhibits marked acidic properties, the β -modification is indifferent to the agent, and has no power to form salts; on remaining in contact with alkalis, however, it dissolves slowly, but the salts produced in this manner yield the α -triketone on acidification. The copper derivative is also that of the latter modification, although Wislicenus (compare this vol., i, 554) has obtained different copper derivatives from the two modifications of ethylic formylphenylacetate.

The two forms of dibenzoylacetylmethane are anhydrous, and

whilst the β -isomeride may be preserved for any period without undergoing change, the α -triketone slowly passes into the neutral form, the transformation being almost complete at the end of three or four months; after the lapse of a year, 100 grams of the α -modification was found on examination to consist of a mixture of 80 grams of the β -triketone, 8 grams of the original form, and 12 grams of dibenzoylmethane. At 85° , the acidic form is converted almost quantitatively into the isomeride, whilst at 110° the reverse transformation takes place to the extent of 75 per cent. of the material employed. When heated at 260 — 280° , both modifications yield dibenzoylmethane and acetic acid. Although β -dibenzoylacetylmethane is prepared by boiling a solution of the isomeride in dilute alcohol, and allowing the liquid to cool spontaneously, this result is not effected when the solution is cooled suddenly, 90 per cent. of the α -triketone under these conditions separating unchanged; either modification, when dissolved in hot absolute alcohol, yields a crystalline mixture of the isomerides, of which the α -form constitutes two-thirds, and the β -triketone one-third. Whilst the action of acetone is exactly similar to that of alcohol (80 per cent. of the α -form being obtained) acetic acid exerts a hydrolytic action, converting the α -triketone into dibenzoylmethane and acetic acid.

Benzoylparabromobenzoylacetylmethane is obtained in the acidic form from benzoylacetone, parabromobenzoic chloride, and potassium carbonate; it crystallises from alcohol in short prisms, and melts at 105 — 106° . Ferric chloride develops an intense red coloration, and copper acetate precipitates the blue *copper* derivative. The neutral modification does not exist.

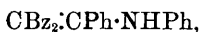
Tribenzoylmethane (compare Claisen, Abstr., 1894, i, 192) occurs in two modifications, the α -form, which melts at 210 — 220° , passing into the β -isomeride, which crystallises in slender needles, and melts at 223 — 226° after sintering at 215° . The spontaneous transformation of α -tribenzoylmethane into the β -form is more rapid than in the case of dibenzoylacetylmethane; 30 per cent. is converted during 20 hours, and the rearrangement is complete at the end of 60 hours, or at 100° after one hour. Treatment with alcohol or acetone converts the α -compound immediately into the β -form, and the transformation is almost as rapid when the substance is covered with methylic alcohol, ether, or glacial acetic acid; the acidic form is more stable, however, in chloroform or benzene, and separates unchanged after dissolution during eight hours.

α -Parabromobenzoyldibenzoylmethane melts at 186 — 189° , and, when the alcoholic solution is boiled, yields the β -modification which melts at 206 — 208° , the conversion of one form into the other being less rapid than in the case of tribenzoylmethane.

Dibenzoylated acetylacetone (Abstr., 1894, i, 31 and 32), the benzoate of benzoyldiacetylmethane, may also be prepared by the alkali carbonate method. When heated with aniline on the water bath it yields the *anilide*, $\text{CAcBz}:\text{CMe}:\text{NHPh}$, which crystallises from methylic alcohol in short, canary-yellow prisms, and melts at 87 — 89° ; it dissolves in alkalis, and is reprecipitated by carbonic anhydride.

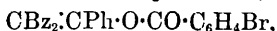
Dibenzoylated benzoylacetone, the benzoate of acetyldibenzoylmethane, has been described as an oil; by the new method, however, it is obtained as a solid substance which crystallises from alcohol in flat, colourless prisms, and melts at 87—88°. The action of alkalis gives rise to dibenzoylacetylmethane and benzoic acid, whilst aniline converts it into the *anilide*, $\text{CBz}_2\text{:CMe:NHPh}$, which crystallises in slender, straw-yellow needles, and melts at 166—167°.

Dibenzoylated dibenzoylmethane, the benzoate of tribenzoylmethane, $\text{CBz}_2\text{:CPh:OBz}$, is prepared from the β -triketone and benzoic chloride (1 mol.) under the influence of sodium carbonate; it is obtained in lustrous, transparent crystals by adding petroleum to the solution in ethylic acetate, and melts at 121—122°. The substance is also produced by the action of benzoic chloride on the sodium derivative of tribenzoylmethane (compare W. H. Perkin, jun., *Trans.*, 1885, **47**, 253), the product of high melting point, which Perkin regarded as tetrabenzoylmethane, not having been obtained in subsequent experiments. The *anilide* of tribenzoylmethane,



is obtained by the action of aniline on the benzoate; it crystallises from alcohol in short, yellow prisms, and melts at 140—142°.

The *parabromobenzoate* of tribenzoylmethane,



crystallises in colourless prisms, and melts at 155—156°. The α -*naphthoate* separates from ethylic acetate, on adding petroleum, in short, lustrous prisms, and melts at 150—151°.

Although the treatment of benzoyldiacetylmethane, dissolved in ethylic acetate, with benzoic chloride in presence of potassium carbonate, gives rise to the benzoate which melts at 102—103° (*Abstr.*, 1894, i, 32), an isomeric compound is produced when the action is carried out with benzoic chloride and pyridine; it crystallises from petroleum in flat, lustrous prisms, and melts at 66—67°, being considerably more soluble than the isomeride. It undergoes conversion into the triketone of higher melting point when heated on the water bath, and after remaining at 120° during 12 hours, 60 per cent. of the material was found to become transformed; both modifications have the molecular weight corresponding with the formula $\text{C}_{19}\text{H}_{16}\text{O}_4$, and neither substance develops a red coloration with ferric chloride. The character of this isomerism is most probably stereochemical, the compounds in question being represented by the formulæ

$\begin{array}{c} \text{Me}\cdot\text{C}\cdot\text{OBz} \\ | \\ \text{Ac}\cdot\text{C}\cdot\text{Bz} \end{array}$ and $\begin{array}{c} \text{Me}\cdot\text{C}\cdot\text{OBz} \\ | \\ \text{Bz}\cdot\text{C}\cdot\text{Ac} \end{array}$; this view is supported by the

fact that under the same conditions of treatment with benzoic chloride, acetyldibenzoylmethane yields but one benzoate, $\begin{array}{c} \text{Me}\cdot\text{C}\cdot\text{OBz} \\ | \\ \text{Bz}\cdot\text{C}\cdot\text{Bz} \end{array}$,

melting at 87—88°, the structure of this substance obviously excluding the possibility of stereoisomerism. Development of this method of benzoylation has revealed the fact that in the case of diketones and ethereal salts of 1:3-diketonic acids, derivatives are invariably obtained in which the benzoic radicle is directly united

with oxygen, whilst the action of benzoic chloride on the alkali derivatives gives rise to benzoates having the acidyl group combined with carbon.

II. [With J. BISHOP TINGLE and C. KERSTIENS.]—As in the case of the triketones already described, the ethereal salts of mesityloxidoxalic acid, $\text{CMe}_2\cdot\text{CH}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{COOH}$, occur in acidic and neutral forms. The latter, distinguished as the β -modifications, are obtained by a general method in which a mixture of mesitylic oxide and the ethereal oxalate is added to ether covering sodium wire; treatment with alcoholic sodium ethoxide converts the neutral into the acidic, or α -modifications.

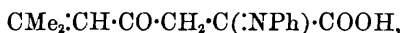
Ethylic β -mesityloxidoxalate, $\text{CMe}_2\cdot\text{CH}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{COOEt}$, is obtained in the manner indicated from mesitylic oxide and ethylic oxalate. It crystallises from petroleum in thin, four-sided plates and short, flat prisms, and melts at $59-60^\circ$; under pressures of 11 mm. and 40 mm. it boils at 143° and 165° respectively, and under atmospheric pressure at $260-263^\circ$. Ferric chloride and ferrous sulphate do not develop coloration with the substance, and no precipitate is formed with zinc or copper acetates; the salt is insoluble in a dilute solution of sodium carbonate, and gaseous ammonia yields no precipitate when led into its ethereal solution. *Methylic β -mesityloxidoxalate* crystallises from petroleum in leaflets, and from ether in short prisms; it melts at 67° , and in its behaviour towards chemical agents resembles the ethylic salt.

β -Mesityloxidoxalic acid is obtained by hydrolysing the ethylic salt, and crystallises from water in tough, vitreous prisms; it melts and evolves gas at $166-167^\circ$, dissolves readily in alcohol and with difficulty in benzene, being moderately soluble in ether, chloroform, and ethylic acetate. Hot aqueous potash resolves it into oxalic acid and mesitylic oxide, the latter being converted into acetone when the treatment with alkali is prolonged.

Ethylic α -mesityloxidoxalate, $\text{CMe}_2\cdot\text{CH}\cdot\text{CO}\cdot\text{CH}\cdot\text{C}(\text{OH})\cdot\text{COOEt}$, is obtained by the action of alcoholic sodium ethoxide on the β -modification, a crystalline specimen being most readily produced by decomposing the copper derivative; it melts at $21-22^\circ$, and, when heated on the water bath, is gradually transformed into the β -salt. The *copper* derivative contains $1\text{H}_2\text{O}$, and crystallises from benzene in dark green, silky needles, which melt and decompose at 165° ; the *ferrous* derivative crystallises in small, blue needles, and the *ferric* derivative separates in brownish-red crystals, and melts at $140-141^\circ$. The *ammonium* derivative is formed when gaseous ammonia is led into the ethereal solution; it is a crystalline powder, and melts at 95° . *Methylic α -mesityloxidoxalate* is produced when the β -salt is treated with sodium methoxide dissolved in methylic alcohol; it crystallises in yellowish prisms, and melts at $83-84^\circ$. In behaviour, it closely resembles the ethylic salt, developing coloration with ferric chloride, ferrous sulphate, and copper acetate; the *ammonium* derivative melts at $78-80^\circ$.

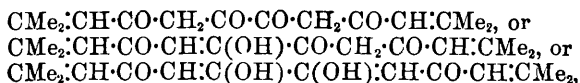
α -Mesityloxidoxalic acid is produced when the β -acid is heated during a short period on the water bath with aqueous soda (2 mols.) or with an alcoholic solution of sodium ethoxide; the most con-

venient method, however, is hydrolysis of the methylic salt. When crystallised from benzene, it contains $1\text{H}_2\text{O}$, and in this condition melts at $92\text{--}93^\circ$, evolving gas at 110° , above which temperature it solidifies, and melts finally at $160\text{--}166^\circ$, the melting point of the β -acid. When heated on the water bath during three or four minutes, it undergoes conversion into the isomeride, the same result being effected on attempting to crystallise the substance from boiling water; the anhydrous acid melts at $84\text{--}86^\circ$, solidifies at 110° , and finally fuses at $164\text{--}166^\circ$, showing that the crystalline hydrated form is not merely the hydrate of the β -acid. Towards ferric chloride, ferrous sulphate and copper acetate, the acid behaves in a manner resembling the ethereal salts. Aniline salts of the two forms are obtained when an alcoholic solution of the base is mixed with the acid, but, in the case of the α -modification, the liquid becomes yellow when heated, and addition of petroleum induces the crystallisation of the *anilido-acid*, $\text{CMe}_2\text{:CH}\cdot\text{CO}\cdot\text{CH}\cdot\text{C}(\text{NHPh})\cdot\text{COOH}$ or



which separates in lustrous, yellow prisms and melts at $120\text{--}121^\circ$; it dissolves readily in alkali carbonates, and the solution in concentrated sulphuric acid is magenta-red.

Oxalaldimesitylic oxide,



is a product of the action of mesitylic oxide (2 mols.) on ethylic oxalate in presence of sodium; it crystallises from alcohol in canary-yellow needles, and melts at $149\text{--}150^\circ$. The substance dissolves readily in dilute alkalis (compare Brühl, this vol., i, 522).

M. O. F.

Action of Thiophenol [Phenylic Hydrosulphide] on Aromatic Diketones. By JULIUS TROEGER and A. EGGERT (*J. pr. Chem.*, 1896, [2], 53, 478—483; compare Abstr., 1885, 748; 1887, 126).—When benzil is heated with twice its weight of thiophenol and zinc chloride for 10 hours on the water bath, deoxybenzoin and phenylic bisulphide are produced. An *additive* compound of quinone and thiophenol, $\text{C}_6\text{H}_4\text{O}_2 + 2\text{C}_6\text{H}_5\cdot\text{SH}$, the analogue of Nietzki's phenoquinone, separates from mixed solutions of quinone and thiophenol in light petroleum; it forms orange-red crystals and is easily sublimed, the quinone being, however, partially separated during the process. Similar products were obtained by substituting parathiocresol and ethylic hydrosulphide for thiophenol.

A. G. B.

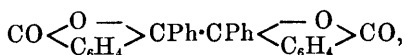
Orthodinitrodibenzylbenzidine and some Derivatives. By FRANCIS E. FRANCIS (*Ber.*, 1896, 29, 1450—1453).—*Orthodinitrodibenzylbenzidine*, $\text{C}_{12}\text{H}_8(\text{NH}\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2)_2$, is prepared by heating benzidine with orthonitrobenzyl chloride in alcoholic solution; it is a red powder, and melts and decomposes at $226\text{--}227^\circ$; the *sulphate*, with $2\text{H}_2\text{SO}_4$, melts and decomposes at 215° . Tin and hydrochloric acid reduce it to benzidine and orthotoluidine, but a small quantity of the

corresponding diamine, melting at 185° , is obtained when the reduction is effected with zinc dust and acetic acid at 20° . The dinitro-compound yields a yellow or red *dinitroso*-derivative, melting at 204° , and a grey *diformyl derivative*, melting at 205° . The latter is reduced by zinc dust and acetic acid at 20° to yellowish-white *diphenylenebisdihydroquinazoline*, $C_{12}H_8(\text{<}\overset{\text{CH}_2}{\text{C}}\text{>}\overset{\text{CH}\cdot\text{NH}}{\text{C}}\text{>}C_6H_4)_2$, melting above 200° ; the *hydrochloride* (with $2HCl$) and *platinochloride* were prepared. C. F. B.

Reduction of Orthobenzoylbenzoic acid. By F. ULLMANN (*Annalen*, 1896, **296**, 17—25).—Rotering reduced orthobenzoylbenzoic acid during 13 days with sodium amalgam, and obtained orthobenzhydrylbenzoic lactone, which further reduction (8—10 days) converts into orthobenzylbenzoic acid, and the same result is brought about when zinc and hydrochloric acid are employed.

The author has attempted to obtain orthobenzylbenzoic acid by reducing orthobenzoylbenzoic acid with hydriodic acid and red phosphorus. On heating the substance in sealed tubes with these agents, however, it becomes completely charred at 160 — 180° , whilst at a lower temperature (140 — 150°), a small quantity of anthracene is produced; at this temperature, hydriodic acid, diluted with its own bulk of water, gives rise almost exclusively to anthracene.

The dilactone of *dihydroxytetraphenylethanedicarboxylic acid*,



is obtained by heating orthobenzoylbenzoic acid with hydriodic acid and yellow phosphorus in a reflux apparatus for four or five hours at 127° in an atmosphere of carbonic anhydride; if the latter condition is not observed, the greater part of the acid remains unaltered, whilst a very small quantity of the lactone is produced, along with anthracene and anthraquinone. It is insoluble in most solvents, but dissolves readily in boiling toluene, aniline, and glacial acetic acid, from which it separates in small plates, melting at 265° . Alkalis convert the lactone into a mixture of orthobenzoylbenzoic and orthobenzhydrylbenzoic acids.

The latter substance is conveniently prepared from orthobenzoylbenzoic acid by reduction with zinc and dilute acetic acid, the lactone separating as the solution cools. Further reduction of the lactone with hydriodic acid and yellow phosphorus converts it into orthobenzylbenzoic acid. M. O. F.

Ethers of Phenolphthaleïn. By ERNESTO GRANDE (*Gazzetta*, 1896, **26**, i, 222—231).—On leaving a mixture of anisoil, phthalic anhydride, and aluminium chloride for several days, driving off the hydrogen chloride at 100° , and pouring into water, a product is obtained, from which soda dissolves anisoilphthaloylic acid (Nourisson, *Abstr.*, 1886, 1029), leaving a residue of the dimethyl ether of phenolphthaleïn, $C_{22}H_{18}O_4$, which von Baeyer prepared by the action of methylic iodide on alkaline phenolphthaleïn (*Abstr.*, 1880, 650), but

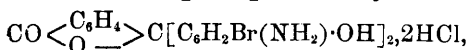
did not describe further. It crystallises in colourless, lustrous laminæ, melting at 101—102°, and is soluble in acetic acid, chloroform, or carbon bisulphide, but insoluble in water; it is precipitated unaltered from its sulphuric acid solution by water, but not if the solution has been heated to 80—90°. It does not react with hydroxylamine, and consequently has the lactonic constitution. When heated with aqueous potash, it is converted into *potassium dimethoxytriphenylcarbinolcarboxylate*, $\text{COOK} \cdot \text{C}_6\text{H}_4 \cdot \text{C}(\text{C}_6\text{H}_4 \cdot \text{OMe})_2 \cdot \text{OH}$, which crystallises in needles, and is soluble in alcohol; when heated above 270°, it decomposes, and a *sublimate*, crystallising in yellow laminæ, melting at 148°, is obtained. On reducing the potassium salt with potash and zinc dust in alcoholic solution, and treating with hydrochloric acid, it gives *dimethoxytriphenylmethanecarboxylic acid*, $\text{COOH} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}(\text{C}_6\text{H}_4 \cdot \text{OMe})_2$, which crystallises in white needles melting at 149—150°, and is soluble in alkali carbonates, concentrated sulphuric acid, ether, benzene, chloroform, or carbon bisulphide. The *barium* salt crystallises in colourless needles containing $3\text{H}_2\text{O}$.

The *dibromo-derivative* of the dimethyl ether of phenolphthaleïn, $\text{C}_{22}\text{H}_{16}\text{Br}_2\text{O}_4$, is obtained by direct bromination, and crystallises in aggregates of colourless needles, melting at 160—161°. W. J. P.

Derivatives of Phenolphthaleïn. By GIORGIO ERRERA and E. BERTÈ (*Gazzetta*, 1896, **26**, i, 264—274).—Dinitrophenolphthaleïn (Hall, *Proc.*, 1893, 14) can be readily obtained by cautiously dropping nitric acid into an alcoholic solution of phenolphthaleïn, and subsequently heating on the water bath; the nitro-compound separates on cooling, and crystallises in yellow needles, melting at 197°.

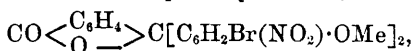
Dibromodinitrophenolphthaleïn, $\text{CO} < \text{C}_6\text{H}_4 \text{O} > \text{C}[\text{C}_6\text{H}_2\text{Br}(\text{NO}_2) \cdot \text{OH}]_2$, $[\text{C} : \text{NO}_2 : \text{OH} : \text{Br} = 1 : 3 : 4 : 5]$, prepared by nitrating tetrabromophenolphthaleïn in a similar manner, crystallises in yellow prisms, melting at 235—236°, is sparingly soluble in the usual solvents, and is not acted on by hydroxylamine. Its *diacetyl* derivative is prepared by the ordinary methods, and forms an amorphous, yellow powder, melting at 145°; it differs from the parent substance in being insoluble in alkalis.

Dinitrophenolphthaleïn is reduced by tin and hydrochloric acid, but neither pure diamidophenolphthaleïn nor its hydrochloride could be isolated. Dibromodinitrophenolphthaleïn also readily undergoes reduction, and *dibromodiamidophenolphthaleïn hydrochloride*,



can be prepared from the product; it crystallises in minute, grey laminæ, decomposing on heating. The free *base* can be obtained as an amorphous, yellow powder, which is soluble in caustic alkalis, reacts with hydroxylamine, and gives a benzoyl derivative.

The *dimethyl* ether of dinitrophenolphthaleïn,



is obtained by heating the sodio- or argento-derivative of the phthalein with methylic iodide; it crystallises in short, yellow needles, melting at 130—132°, and is insoluble in alkalis or their carbonates. It is accompanied by the corresponding *monomethyl ether*, $C_{21}H_{14}N_2O_8$, which is a yellow, amorphous powder, melts at 90—92°, and dissolves readily in alkalis or alkali carbonates. On reducing the dimethyl ether with tin and hydrochloric acid, it yields the *dimethyl ether* of diamidophenolphthalein, $C_{22}H_{20}N_2O_8$, as a white, amorphous powder; when treated with nitrous acid, it is not converted into guaiacolphthalein, but into a *substance* of the composition $C_{22}H_{16}N_2O_{10}$. W. J. P.

Introduction of a Fourth Radicle in place of the Hydroxyl Group of Triphenylcarbinol. By KARL WEISSE (*Ber.*, 1896, **29**, 1402—1404).—Triphenylthienylmethane melts at 237°, not at 239° as previously stated (*Abstr.*, 1895, i, 543). It is converted by bromine into a *monobromo-derivative*, which crystallises in long needles, and melts at 191—192°. It has not been found possible to bring about condensation between triphenylcarbinol and benzene, anisoil, toluene, or naphthalene by the method employed with thiophen. Homologues of thiophen, on the other hand, undergo the reaction readily. *Methylthienyltriphenylmethane* melts at 181—182°, whilst *ethylthienyltriphenylmethane* melts at 111°. Monochlorothiophen also readily undergoes condensation, forming *chlorothieryltriphenylmethane*, which melts at 204—205°. The corresponding *iodo-compound* can also be readily obtained, and melts at 184—185°, whilst dibromo- and nitro-thiophen do not react. Thiophen, moreover, does not appear to react with trinitrotriphenylcarbinol.

A. H.

Constitution of Colour Bases of the Triphenylmethane Series. By HUGO WEIL (*Ber.*, 1896, **29**, 1541—1542).—The results of von Georgievics (this vol., i, 441) are not in accordance with those obtained by the author in a research which he is at present unable to complete.

C. F. B.

Bidiphenylenethylene and Bidiphenylenethane. By CARL GRAEBE and H. STINDT (*Annalen*, 1896, **291**, 1—8; compare *Abstr.*, 1893, i, 38, and this vol., i, 442).—The authors describe in some detail the method devised for the production of bidiphenylenethylene from fluorene and lead oxide (*loc. cit.*). Fusion with potash converts the red hydrocarbon into orthodiphenylcarboxylic acid, whilst hot, concentrated nitric acid, mixed with glacial acetic acid, gives rise to *dinitrobidiphenylenethane*, $\begin{matrix} C_6H_4 \\ | \\ C_6H_4 \end{matrix} > C(NO_2) \cdot C(NO_2) < \begin{matrix} C_6H_4 \\ | \\ C_6H_4 \end{matrix}$, which crystallises in long, yellow needles, and melts, evolving gas, at 184—185°. The bromide of bidiphenylenethylene has been already described as yielding the red hydrocarbon on treatment with sodium, and bidiphenylenethane under the influence of alcoholic potash; the latter agent, if allowed to act during a sufficiently long period, also gives rise to the red hydrocarbon.

Bidiphenylenethylene oxide, $\begin{array}{c} \text{C}_6\text{H}_4 \\ | \\ \text{C}_6\text{H}_4 \end{array} > \begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{C} - \text{C} \end{array} < \begin{array}{c} \text{C}_6\text{H}_4 \\ | \\ \text{C}_6\text{H}_4 \end{array}$, is obtained by heating the bromide with water at 150° ; it separates from carbon tetrachloride in colourless crystals, and melts at 258° . The *acetate* of bidiphenylenethylene glycol, $\begin{array}{c} \text{C}_6\text{H}_4 \\ | \\ \text{C}_6\text{H}_4 \end{array} > \text{C}(\text{OAc}) \cdot \text{C}(\text{OAc}) < \begin{array}{c} \text{C}_6\text{H}_4 \\ | \\ \text{C}_6\text{H}_4 \end{array}$, is produced on heating a solution of the bromide in benzene with silver acetate in a reflux apparatus; it separates from glacial acetic acid in colourless crystals, and melts, becoming red and decomposing, at 230° . The *glycol* is obtained on heating the acetate with baryta at 140° ; it crystallises from alcohol in colourless needles, and melts at 237° .

The observation that bidiphenylenethane is the initial product of the action of heated lead oxide on fluorene, has led the authors to prepare the hydrocarbon in this manner, instead of by the action of sodium amalgam on the red hydrocarbon; it is also produced when fluorene and fluorenone are heated with sodium acetate at 310° and subsequently at 340 – 350° . Oxidation with sodium dichromate in glacial acetic acid gives rise to fluorenone. M. O. F.

Formation of Dinitronaphthalenes. II. By CH. GASSMANN (*Ber.*, 1896, **29**, 1521–1522; compare this vol., i, 486).—The formation of 1:4'- and 1:1'-dinitronaphthalene is evidently a function of the temperature, 1:1'-dinitronaphthalene is formed at the lowest possible temperature, especially at the commencement of nitration, and the yield is improved by allowing the reaction to proceed slowly. Heating towards the end of the reaction does not appear to improve the yield.

1:4'-Dinitronaphthalene, on the contrary, is best formed at a high temperature; the presence of concentrated acid is here of advantage. The author is still engaged in investigating the production of peridinitronaphthalene (*loc. cit.*). J. F. T.

Influence of Substituents on the Formation of Quinoximes. By FRIEDRICH KEHRMANN and M. HERTZ (*Ber.*, **29**, 1415–1420).—The *oxime* of hydroxynaphthaquinoneimide, $\text{C}_{10}\text{H}_5\text{N}_2\text{O}_2$, exists in a red and yellow modification. The yellow modification crystallises from alcohol in bright yellow, silky needles, and melts and decomposes at about 200° ; it dissolves very slowly in cold, dilute soda, forming a bright yellow solution, which on acidification with acetic acid, assumes a brick-red hue, and on subsequent evaporation, deposits the oxime in needles of that colour; the latter, unlike the yellow needles, dissolve quickly in dilute soda, and, when heated with water, dissolve, forming a red solution, which rapidly becomes yellow, and then deposits the yellow modification.

The oxime is reduced by a warm solution of stannous chloride in alcoholic hydrogen chloride, and the resulting colourless solution sets to a mass of needles, consisting of 1:4-diamido-2-naphthol *dihydrochloride*, $\text{C}_{10}\text{H}_5(\text{NH}_2)_2 \cdot \text{OH} \cdot 2\text{HCl}$; the latter is obtained on passing

hydrogen chloride into its aqueous solution in the form of beautiful, long, colourless needles, which on preservation become tinted superficially with violet; when warmed with acetic anhydride and anhydrous sodium acetate, it gives the *diacetyl* derivative, $C_{10}H_5(NHAc)_2OH$, which possesses a marked phenolic character; this crystallises from acetic acid in colourless, granular crystals, and melts and decomposes at $250-260^\circ$. The ammoniacal solution of the hydrochloride is coloured by exposure to the atmosphere, the free base being thus oxidised. The product, 2:1:4-*hydroxynaphthaquinonediiimide*, $C_{10}H_5(NH)_2OH$, is precipitated in brownish-yellow needles; it is readily reduced to diamido- β -naphthol by stannous chloride, and dissolves in alcohol, forming a yellow solution, which, when warmed, becomes red, and on cooling deposits crystals of hydroxynaphthoquinoneimide; the latter is also produced from the diimide by the action of hot dilute hydrochloric acid.

2:4:1-*Amidonaphthaquinoneoxime*,



is precipitated from alkaline solution by dilute acetic acid; it crystallises from alcohol in glistening yellow needles, and decomposes at $220-230^\circ$. It is reduced by means of stannous chloride to 1:2:4-amidodihydroxynaphthalene.

The existence of two modifications of hydroxynaphthaquinoneimide is best explained by assuming that the following formulæ represent the modifications stable in presence of alkali and acid

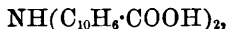
respectively, $C_6H_4 \begin{smallmatrix} C(NOH) \cdot C \cdot OH \\ | \\ C(HH) - CH \end{smallmatrix}$, and $C_6H_4 \begin{smallmatrix} C(NOH) \cdot CO \\ | \\ C(NH_2) : CH \end{smallmatrix}$. Ana-

logous constitutions are suggested for Henrich's two modifications of nitroso-orcinol (this vol., i, 476). A. L.

Naphthalene-1:4'-dicarboxylic acid and its Derivatives. By PIETRO MORO (*Gazzetta*, 1896, **26**, i, 89—116).—1:4'-*Dicyanonaphthalene*, $C_{10}H_6(CN)_2$, is prepared from 1:4'-naphthalenediamine sulphate by carefully diazotising in hydrochloric acid solution, not allowing the temperature to rise above 0° , and converting the diazo-compound into the dicyano-derivative by the Sandmeyer reaction; it crystallises in white needles, melting at $266-267^\circ$ (corr.), and is insoluble in water, but soluble in alcohol, ether, or acetic acid. On hydrolysis, preferably by prolonged boiling with alcoholic potash, but also by heating in a sealed tube with concentrated hydrochloric acid, or by treating with sulphuric acid, it is converted into *naphthalene-1:4'-dicarboxylic acid*; this is white and crystalline, and decomposes without melting at above 286° . The *ammonium* salt and the *calcium* salt, with $1H_2O$, crystallise in brownish prisms, whilst the *silver* salt forms a slightly coloured powder; the *barium* salt, with $3\frac{1}{2}H_2O$, crystallises in reddish prisms; the *methylic* salt in brownish laminæ, melting at $114-115^\circ$ (corr.); and the *ethylic* salt in white needles, melting at $123-124^\circ$ (corr.). The acid *chloride*, $C_{10}H_6(COCl)_2$, prepared by the action of phosphorus pentachloride on the acid, crystallises in white prisms, melting at $155-156^\circ$ (corr.); on heating with

phenol it yields the *diphenylic* salt, $C_{10}H_6(COOPh)_2$, which forms a crystalline mass, melting at $198-199^\circ$ (corr.).

On heating the ammonium salt, it yields 1 : 4'-dicyanonaphthalene, and a substance which crystallises in white needles, decomposing above 240° , and seems to have either the constitution



or $NH(CO \cdot C_{10}H_6 \cdot COOH)_2$. The *silver* salt is a white crystalline powder, the *calcium* salt, with $3H_2O$, crystallises in yellow laminæ, and the *barium* salt forms yellow pyramids. The *amide* of the naphthalenedicarboxylic acid is obtained as a yellowish, amorphous powder, insoluble in the ordinary solvents, on boiling the acid chloride with ammonium carbonate solution.

Trinitronaphthalene-1 : 4'-dicarboxylic acid, $C_{10}H_3(NO_2)_3(COOH)_2$, may be prepared by direct nitration of the acid in presence of sulphuric acid, and is a yellow powder, soluble in ether, alcohol, or acetic acid; its *ethylic* salt crystallises in brown pyramids, melting at $152-153^\circ$ (corr.), and the *barium* salt, with $2H_2O$, in brownish needles.

Dinitronaphthalene-1 : 4'-dicarboxylic acid, $C_{10}H_4(NO_2)_2(COOH)_2$ prepared by nitrating the carboxylic acid with boiling fuming nitric acid, is a yellow, crystalline powder; its *ethylic* salt crystallises in white laminæ, melting at 160° , with incipient decomposition, and the *methylic* salt in brown prisms, melting and decomposing at $210-215^\circ$. The *ammonium* salt could only be obtained as a resinous mass, and the *calcium* salt crystallises with $4\frac{1}{2}H_2O$ in yellow prisms.

On nitrating the amide with boiling fuming nitric acid, an *isomeride* of the above dinitronaphthalene-1 : 4'-dicarboxylic acid is obtained; it crystallises in yellow prisms, which decompose on heating, and gives a crystalline *ethylic* salt, melting at $253-254^\circ$ (corr.) with decomposition.

Two substances, melting at $184-205^\circ$ and at $157-165^\circ$ respectively, are obtained by oxidising naphthalene-1 : 4'-dicarboxylic acid with potassium permanganate; these are still under investigation.

Tetrahydronaphthalene-1 : 4'-dicarboxylic acid, $C_{10}H_{10}(COOH)_2$, is prepared by reducing the naphthalenedicarboxylic acid with sodium amalgam; it crystallises in needles, melting at $237.5-238.5^\circ$ (corr.), and decolorises alkaline permanganate in the cold. The *calcium* salt, with $3\frac{1}{2}H_2O$, and the *barium* salt, with $1H_2O$, crystallise in nearly white laminæ, but the ammonium, ethylic, and methylic salts could not be obtained in the crystalline form.

Sulphonaphthalene-1 : 4'-dicarboxylic acid, $C_{10}H_5(COOH)_2 \cdot HSO_3$, is prepared by heating the dicarboxylic acid with sulphuric acid in closed tubes at $190-200^\circ$; it forms a crystalline, deliquescent, yellow mass, which begins to decompose at 275° , and yields a crystalline *barium* salt containing $2H_2O$.

W. J. P.

Isomeric Naphthalene Derivatives. III. By PAUL FRIEDLÄNDER and HERMANN RÜDT (*Ber.*, 1896, 29, 1609—1613; compare *Abstr.*, 1895, i, 668).—1 : 3-*Amidonaphthol-4-sulphonic acid* is obtained by treating 1 : 3-amidonaphthol with sulphuric acid at the ordinary temperature. The solutions of the alkali salts show a faint green fluorescence.

When it is heated with water or dilute sulphuric acid at 120° , it yields 1:3-dihydroxynaphthalene (naphtharesorcinol), which crystallises in lustrous plates, and melts at 124° . The acetyl compound melts at 56° . It is distinguished from the other isomerides by the fact that it forms naphthaflorescein (German Patent, 84,990), when heated with phthalic anhydride and zinc chloride. When treated in acetic acid solution with nitrosodimethylaniline, 1:3-dihydroxynaphthol is converted into a reddish-violet colouring matter. The azo-derivatives closely resemble those of resorcinol. When 1:3-dihydroxynaphthol is heated with aqueous soda at 180 – 190° , it is converted quantitatively into orthotoluic and acetic acids. It is less readily attacked by fused soda. When it is treated with ammonia or amines, the β -hydroxyl group is first attacked. Ammonia yields 3:1-amidonaphthol, together with a little 1:3-naphthylenediamine. Aniline converts it into phenylamidonaphthol, the alkaline solution of which rapidly absorbs oxygen from the air, with formation of naphthaquinonanil. 1:3-Dihydroxynaphthol-3'-sulphonic acid is obtained by heating the corresponding amidonaphtholsulphonic acid (German Patent, 82,676) with water at 120° ; its sodium salt forms white needles. The azo-derivatives of this acid are yellow to yellowish-red.

A. H.

Unsaturated Sulphones of the Naphthalene Series. By JULIUS TROEGER and K. ARTMANN (*J. pr. Chem.*, 1896, [2], 53, 484–500; compare Otto, *Abstr.*, 1895, i, 229).— β -Naphthylallylsulphone, $C_3H_5 \cdot SO_2 \cdot C_{10}H_7$, is prepared by heating a β -naphthalenesulphinate with excess of allylic bromide in a reflux apparatus, distilling the excess of bromide, extracting the residue with water, and crystallising from alcohol; it forms long, white needles, melts at 95° , and dissolves in alcohol, ether, glacial acetic acid, benzene, and methylic alcohol, but not in water. When heated at 150° with water or aqueous alkali, the sulphone takes up a molecule of water, yielding the hydroxypropyl- β -naphthylsulphone described below. Nascent hydrogen is without action on the sulphone; bromine in glacial acetic acid converts it into the dibromide, $CH_2Br \cdot CHBr \cdot CH_2 \cdot SO_2 \cdot C_{10}H_7$, which crystallises in slender, white needles, melts at 85° , and dissolves in alcohol, ether, glacial acetic acid, and ethylic acetate, but not in water. When this dibromide is heated with water, it yields an oxygen derivative, $C_3H_5O \cdot SO_2 \cdot C_{10}H_7$, which appears to be an anhydride of the corresponding glycol; it forms white crystals, and melts at 167° .

β -Naphthylbromopropylsulphone may be obtained by heating the sulphone with a saturated solution of hydrogen bromide in glacial acetic acid at 120° ; it forms white, granular crystals, melts at 124° , and dissolves freely in alcohol and glacial acetic acid, sparingly in ether, but not in water. Water at 150° converts this bromo-derivative into the corresponding β -naphthylhydroxypropylsulphone,



which forms white, granular crystals, and melts at 137° . Alcoholic potash debrominates it, yielding the parent sulphone.

β -Naphthylidopropylsulphone is analogously prepared, and crystallises in white needles, melting at 106° , and freely soluble in alcohol, glacial acetic acid, and ethylic acetate, sparingly in ether, and not in light petroleum; its behaviour in water is similar to that of the bromo-derivative.

β -Dinaphthylpropylenedisulphone, $C_{10}H_7 \cdot SO_2 \cdot CHMe \cdot CH_2 \cdot SO_2 \cdot C_{10}H_7$, from propylenic bromide and a β -naphthalenesulphinic acid, crystallises in lustrous, white laminae, and melts at 123° .

Trimethylene- β -dinaphthylsulphone, $CH_2(CH_2 \cdot SO_2 \cdot C_{10}H_7)_2$, analogously prepared, is white, and melts at 145° .

β -Trinaphthylallyltrisulphone, $C_{10}H_7 \cdot SO_2 \cdot CH(CH_2 \cdot SO_2 \cdot C_{10}H_7)_2$, from allylic tribromide and a β -naphthalenesulphinic acid, is a white, flocculent substance, which melts at 230° , and is sparingly soluble; from the mother liquor of this compound, a white sulphone crystallises, which melts at 157° , and is also obtained by heating β -naphthylallylsulphone dibromide with a β -naphthalenesulphinic acid in alcoholic solution; the authors are disposed to regard this sulphone as a stereoisomeride of β -dinaphthylpropylenedisulphone, which has an asymmetric carbon atom (compare Otto, *loc. cit.*).

β -Naphthylphenylpropylenedisulphone, $SO_2Ph \cdot CHMe \cdot CH_2 \cdot SO_2 \cdot C_{10}H_7$, is prepared by heating a benzenesulphinic acid with β -naphthylallylsulphone dibromide in alcoholic solution; it crystallises in aggregates of needles, and melts at 123° . The behaviour of β -naphthylallylsulphone dibromide to β -naphthylhydrosulphide is described, the chief product being the thio-ether, $C_3H_5(SC_{10}H_7)_2 \cdot SO_2 \cdot C_{10}H_7$, which melts at 129° .

Allyl- α -naphthylsulphone crystallises in monoclinic prisms, and melts at 67° .
A. G. B.

Dianthranol. By WILLIAM R. ORNDORFF and C. L. BLISS (*Amer. Chem. J.*, 1896, **18**, 453—465).—A solution of anthranol in benzene was exposed to bright sunlight for some weeks, when the solution became successively dark green, yellow, and reddish-yellow, and white and reddish-yellow crystals separated, which were decolorised by bone-black, and purified by recrystallisation from acetone. The dianthranol, $C_{28}H_{20}O_2$, prepared in this way, crystallises in colourless, tabular, or columnar crystals, melts and decomposes at about 250° , and is very soluble in chloroform, less so in acetone, glacial acetic acid, and benzene, slightly soluble in alcohol, and almost insoluble in benzene. Solutions of the alkalis fail to dissolve dianthranol even when boiled, so that the compound may be separated from anthranol in this way. When a benzene solution of dianthranol is allowed to evaporate in air, partial oxidation to anthraquinone occurs. When heated in sulphuric acid at its melting point, dianthranol undergoes partial conversion into anthranol. The molecular weight of anthranol was determined by the cryoscopic method, and agreed with the formula $C_{14}H_{10}O$; the compound crystallises in the rhombic system, whilst dianthranol is monoclinic; crystallographical measurements of each are given.

Dianthranol is also formed when a solution of anthranol in benzene is boiled for 12 hours, and when air is passed through a solution of

anthranol in potash. *Diacetyldianthranol* crystallises in light yellow plates, and melts and decomposes at 276—279°; it is very soluble in chloroform, and sparingly in benzene and alcohol. The authors consider that dianthranol consists of two molecules of anthranol, which are united by the broken para-linkings between the two γ -carbon atoms in each molecule (compare this vol., i, 176). A. G. B.

Terpenes and Ethereal Oils. By OTTO WALLACH (*Annalen*, 1896, 291, 342—367).—I. [With G. M. KERR.]—Experimental details are now described respecting the neutral oxidation product of terpineol having the composition $C_{10}H_{16}O_3$ (Abstr., 1895, i, 547). The constitution of this substance, and its relation to terpenylic acid, have been already discussed (*loc. cit.*).

II. [With HENRY V. ARNY.]—The conversion of terpineol into carvone was first effected by obtaining carveol methyl ether from terpineol tetrabromide under the influence of sodium methoxide, and oxidising it with chromic anhydride (Abstr., 1895, i, 59). A more direct method is now described, terpineol nitrosochloride being converted into a hydroxy-oxime, which yields inactive carvone under the influence of dilute sulphuric acid.

Hydroxydihydrocarvoxime, $OH \cdot C_{10}H_{15} \cdot NOH$, is obtained from terpineol nitrosochloride by the action of sodium ethoxide (1 mol.); it crystallises from ethylic alcohol, and melts at 133—134°. The *diacetyl* derivative crystallises from ethylic acetate, and melts at 107°. Dilute sulphuric acid converts hydroxydihydrocarvoxime into inactive carvone, and concentrated sulphuric acid gives rise to amidothymol (compare Abstr., 1894, i, 537).

III. [With RICHARD GUERICKE.]—The *dibromide* of pinole hydrate, 1:6:2:8-*dibromodihydroxyhexahydrocymene*, is prepared by adding a solution of bromine in chloroform to pinole hydrate in the same medium; it melts at 131—132°.

The *anhydride* of pinole glycol, $C_{10}H_{16}O_2$, is obtained by the action of sodium methoxide on the foregoing dibromide; whilst the latter is unsaturated, the new substance is saturated, and has the constitution $O < \begin{array}{c} CH \cdot CH_2 \cdot CH \\ | \quad \quad | \\ CMe \quad \quad CH \end{array} > CH_2 \cdot \begin{array}{c} CMe_2 \\ | \\ O \end{array}$. The anhydride is an oil which boils at 206—207°, and at 82° under a pressure of 12 mm.; the sp. gr. = 1.0335 at 20°, and the refractive index, $n_D = 1.4588$ at 20°. Hydrolysis converts the substance into pinole glycol, and it is, therefore, a true anhydride of that substance.

According to the view which regards pinole hydrate as an unsaturated substance containing two hydroxyl groups, of which one is united with a secondary and the other with a tertiary carbon atom, oxidation should give rise to a hydroxy-ketone.

Hydroxydihydrocarvone, $CMe < \begin{array}{c} CO \cdot CH_2 \\ | \quad \quad | \\ CH \cdot CH_2 \end{array} > CH \cdot CMe_2 \cdot OH$, is obtained by oxidising pinole hydrate with chromic acid in glacial acetic acid. The *semicarbazone* melts at 174°, and the *oxime* crystallises from ethylic alcohol, and melts at 134°.

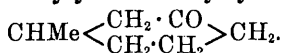
The original method of obtaining terpinolene from terpineol (Wallach and Kerkhoff, Abstr., 1893, i, 595) was modified by von

Baeyer (Abstr., 1894, i, 253). The author now prepares it with great facility by dissolving terpineol in anhydrous formic acid, and gently heating the liquid for a few minutes, when terpinolene rapidly separates.

It has been stated (Abstr., 1893, i, 595) that dipentene is produced when terpineol is heated at 180—190° with solid potassium hydrogen sulphate. The same result is effected in the presence of much water when the operation is performed at 250°, this temperature being maintained during six hours.

The author discusses the constitution of pinene, and criticises the conclusions at which Wagner has arrived (compare Abstr., 1894, i, 610). M. O. F.

Condensation Products of Cyclic Ketones: Syntheses in the Terpene Series. By OTTO WALLACH (*Ber.*, 1896, 29, 1595—1601).—The author has already shown (this vol., i, 309) that on hydrolysis, pulegone readily yields methylcyclohexenone,



Subsequent investigation has shown that this substance lends itself to the synthesis of numerous compounds, the production of which depends on condensation.

The *bicyclic ketone*, $\text{C}_{14}\text{H}_{22}\text{O}$, is obtained in the form of the *hydrochloride*, $\text{C}_{14}\text{H}_{23}\text{OCl}$, melting at 90° when hydrogen chloride is led into methylhexenone, and the *hydrobromide*, $\text{C}_{14}\text{H}_{23}\text{OBr}$, which melts at 90—91°, is produced when hydrogen bromide is employed; the action of hot aniline on these compounds liberates the ketone, which boils at 143—144° under a pressure of 10 mm. The *oxime* melts at 120°, and yields, on reduction, the *base* $\text{C}_{14}\text{H}_{23}\text{NH}_2$, which melts at 50°, and boils at 165—166° under a pressure of 20 mm.; the *hydrochloride* and *platinochloride* are crystalline, and the *nitrate* is sparingly soluble in nitric acid. The constitution of the ketone is probably represented by the formula $\text{CH}_2 < \begin{matrix} \text{CHMe} \cdot \text{CH}_2 \\ \text{CH}_2 - \text{CH}_2 \end{matrix} > \text{C} : \text{C} < \begin{matrix} \text{CO} - \text{CH}_2 \\ \text{CHMe} \cdot \text{CH}_2 \end{matrix} > \text{CH}_2.$

Benzylidenemethylhexenone, $\text{C}_7\text{H}_{10}\text{O} : \text{CHPh}$, is produced on adding alcoholic sodium ethoxide to a mixture of methylhexenone and benzaldehyde (1 mol.), and is precipitated on adding water to the liquid; it crystallises from ether, and melts at 59°, boiling at 190—200° under a pressure of 13 mm. The *oxime* crystallises from dilute alcohol in colourless, transparent prisms, and melts at 109—110°.

Dibenzylidenemethylhexenone, $\text{C}_7\text{H}_8\text{O}(\text{CHPh})_2$, is obtained by the same method as the foregoing substance, 2 mols. of benzaldehyde being employed; it crystallises from alcohol in small, intensely yellow needles, and melts at 126—128°.

Methylcyclohexenone also combines with other aldehydes, for example, nitrobenzaldehyde and cinnamaldehyde; with acetone it yields the compound $\text{C}_{10}\text{H}_{16}\text{O}$, which closely resembles pulegone, and is isomeric with it. The remarkable activity of methylhexenone most likely depends on the unsubstituted condition of the methylene group in juxtaposition to the carbonyl; and, on this assumption, the behaviour of cyclic ketones towards benzaldehyde presents a more

convenient indication of their constitution than the production of hydroxymethylene derivatives. An investigation in this direction has given rise to the following compounds.

Benzylidenementhone, $\text{CHMe}_2\text{CH} < \begin{smallmatrix} \text{CH}_2 \\ \text{CO}\cdot\text{C}(\text{CHPh}) \end{smallmatrix} > \text{CHMe}$, is obtained in the form of the *hydrochloride* melting at 140° , when hydrogen chloride is led into a mixture of menthone and benzaldehyde (1 mol.); the compound boils at $188\text{--}189^\circ$ under a pressure of 12 mm., and the *hydrobromide*, which is crystalline, melts and decomposes at $115\text{--}116^\circ$. The *oxime* is sparingly soluble in alcohol and ether, crystallising from these agents in woolly needles, which melt at $160\text{--}161^\circ$.

Benzylidenepulegone boils at $202\text{--}203^\circ$, under a pressure of 12 mm. Carvone also combines with benzaldehyde, yielding a solid condensation product.

Benzylidene-eucarvone, $\text{C}_{10}\text{H}_{12}\text{O}:\text{CHPh}$, separates in measurable crystals, and melts at $112\text{--}113^\circ$; along with it is produced a *compound*, which crystallises from a mixture of chloroform and alcohol in snow-white leaflets, and melts at $193\text{--}194^\circ$.

Dibenzylidenesuberone, $\text{C}_7\text{H}_8\text{O}(\text{CHPh})_2$, separates from alcohol in colourless crystals, and melts at $107\text{--}108^\circ$.

Dibenzylidenemethylpentenone, $\text{C}_6\text{H}_6\text{O}(\text{CHPh})_2$, is obtained from benzaldehyde (2 mols.) and β -methylketopentamethylene (Abstr., 1893, i, 130), and separates from alcohol in yellow crystals which melt at $149\text{--}151^\circ$. The methylpentenone also combines with acetone, and the *oxime* of the condensation product melts at $85\text{--}87^\circ$.

M. O. F.

Root of *Rumex Nepalensis* (Wall.). By OSWALD HESSE (*Annalen*, 1896, 291, 305—312).—The astringent principle occurring in the root of *Rumex nepalensis* (Wall.), has been attributed to chrysophanic acid; the author having shown that chrysophanic acid obtained from *Parmelia parietina* differs from that derived from rhubarb, has studied the root in question, and isolated from it three new substances, one of which, rumicin, is isomeric with, and closely resembles, chrysophanic acid, but is not identical with it.

Rumicin, $\text{C}_{15}\text{H}_{10}\text{O}_4$, crystallises from light petroleum in golden-yellow leaflets with metallic lustre, and melts at $186\text{--}188^\circ$; the solution in caustic potash is purple-red, becoming colourless on exposure to carbonic anhydride, which precipitates rumicin. When heated with hydriodic acid, it yields chrysophanohydroanthrone, which is obtained from chrysophanic acid under the influence of the same agent (Abstr., 1895, i, 292).

Nepalin, $\text{C}_{17}\text{H}_{14}\text{O}_4$ (compare this vol., i, 315), crystallises from glacial acetic acid in microscopic, orange needles, and melts at 136° ; it is insoluble in alkali carbonates, but dissolves in caustic potash, forming a purple solution, which becomes colourless under the influence of carbonic anhydride. The solution in concentrated sulphuric acid is blood-red. The *diacetyl* derivative crystallises from glacial acetic acid in lustrous, brownish-yellow rhombohedra, which darken at 170° , and melt at 181° .

Nepodin, $\text{C}_{18}\text{H}_{16}\text{O}_4$, crystallises from a mixture of benzene and

light petroleum in long, greenish-yellow prisms, and melts at 158° . It dissolves readily in alkali carbonates, forming a yellowish-brown solution; the solution in concentrated sulphuric acid is an intense, yellowish-red colour. The *diacetyl* derivative crystallises in pale yellow rhombohedra, darkens at 180° , and melts and decomposes at 198° .

These three constituents of *Rumex nepalensis*, of which nepalin greatly preponderates, are separated from one another by extracting the root with ether, removing nepodin by means of aqueous potassium carbonate, evaporating the ether, and extracting the rumicin from the residue with boiling acetone; the nepalin remaining undissolved.

M. O. F.

Chlorophyll. By EDWARD SCHUNCK and LEO MARCHLEWSKI (*Ber.*, 1896, **29**, 1347—1352).—Tschirch has recently (*Ber. deut. bot. Gesell.*, 1896, 76) questioned some of the authors' previous conclusions on this subject. They contest the accuracy of his results, and give an account of the present state of our knowledge of the chemistry of chlorophyll. By the action of hydrochloric acid, chlorophyll yields phylloxanthin, and this, by the further action of the acid, is converted into phyllocyanin; chlorophyll shows two absorption bands, phylloxanthin four, and phyllocyanin five. It has been found, not only in this case, but with all other chlorophyll derivatives, that the number of absorption bands increases as the chlorophyll complex is resolved. Tschirch regards phylloxanthin as a derivative of phyllocyanin; that this is incorrect is readily proved by shaking an ethereal solution of the former with hydrochloric acid, when it is quickly changed into the latter. The authors suggest that Tschirch's "phyllocyanic acid" is really impure phyllocyanin, as the absorption spectra are almost identical. "Phyllopurpuric acid," which he obtained by heating alkachlorophyll with alkali, is a mixture, one constituent being phylloporphyrin, $C_{16}H_{18}N_2O$, which is closely related to hæmatoporphyrin, $C_{16}H_{18}N_2O_3$, both in composition and in spectroscopic properties; these are best observed in ethereal, not in alcoholic, solution. An important step in the investigation of the constitution of chlorophyll was made when it was recognised as a pyrroline derivative.

J. B. T.

Phenylcoumalin. By J. A. LEBEN (*Ber.*, 1896, **29**, 1673—1680).—Phenylcoumalin is readily purified by Ciamician and Silber's method (*Abstr.*, 1895, i, 554).—The best yield of the polymeric compound, $(C_{11}H_8O_2)_2$, is obtained by heating phenylcoumalin with concentrated hydrochloric acid at 110° during about 24 hours; the molecular weight was determined by the cryoscopic method in benzoic acid. No polymeride of phenyldimethylcoumalin could be prepared. δ -Phenylvaleric acid is formed by the reduction of phenylcoumalin by means of sodium amalgam, but hydriodic acid in acetic acid solution gives much better results. Phenylcoumalin forms additive compounds with various substances containing a phenylic group; they crystallise readily, but dissociate in solution. The *picric acid* and *salicylic acid* derivatives melt at 81 – 82° and 93° respectively. *Phenyldimethylcoumalin-quinol* crystallises in small, colourless needles,

melting at 113° . *Phenylcoumalin-dianiline*, $C_{11}H_8O_2 \cdot 2NH_2Ph$, crystallises with benzene in slender, colourless, stellate needles, melting at $115-118^{\circ}$; when dried, the compound becomes yellow; from alcohol, yellow nodular aggregates are deposited, melting at 142° . The yield is 70 per cent. of the phenylcoumalin employed.

When heated with concentrated hydrochloric acid, the aniline derivative yields 1 : 2-diphenyl-6-pyridone, crystallising in colourless, slender, reticular needles, melting at $144-146^{\circ}$.

2-Phenyl-6-pyridone, $C_{11}H_9ON$, is prepared by the interaction of phenylcoumalin and ammonium acetate; it crystallises in small, yellow plates, melting at 197° . The hydrochloride crystallises in small, pale yellow needles, melting at 104° ; like the aurochloride and platinochloride, it is dissociated by water.

2-Phenylpyridine is formed by the distillation of the pyridone with zinc dust; the picrate melts at 175° , not at $169-172^{\circ}$, as stated by Skraup and Cobenzl; the platinochloride crystallises with $2H_2O$, in long, orange needles, melting at 204° . 2 : 6-Phenylchloropyridine, prepared by the action of phosphorus chloride on the pyridone at 150° , crystallises in colourless needles, melts at 34° , and is readily soluble in concentrated, but not in dilute, hydrochloric acid. The aurochloride crystallises in pale yellow needles.

These results confirm the formula, $CH \begin{smallmatrix} \text{CH:CPH} \\ \text{CH-CO} \end{smallmatrix} > O$, which Ciamician and Silber had previously suggested for phenylcoumalin; they show that Hesse's statements with regard to the purification of this compound are incorrect, and throw doubt on the existence of "oxy-phenylcoumalin" which he has described. J. B. T.

Synthesis of Carbazole. By CARL GRAEBE and F. ULLMANN (*Annalen*, 1896, 291, 16--17).—The action of nitrous acid on orthamidodiphenylamine converts it into phenylazimidobenzene, and when this substance is heated in a distilling flask at 360° , copious evolution of nitrogen occurs, and carbazole distils over almost free from phenylazimidobenzene. M. O. F.

New Derivatives of Phenyltrimethylpyrazolone. By M. C. SCHUTTEN (*Chem. Centr.*, 1895, ii, 34; from *Maandbl. natuurw.*, 19, 93—101).—Phenyltrimethylpyrazolone thiocyanate, $C_{11}H_{12}N_2O \cdot HSCN$, is best obtained by evaporating a solution of antipyrine and potassium thiocyanate in molecular proportions, and then adding concentrated hydrochloric acid; it crystallises in small, compact needles, which turn red when exposed to the air; melts at $121-122^{\circ}$, and is only sparingly soluble in cold water and ether, readily in hot water, alcohol, and benzene. When strongly heated, it decomposes, and yields obnoxious vapours. Its solutions give with ferric chloride a flocculent, red precipitate, consisting of ferric phenyltrimethylpyrazolone thiocyanate, $(C_{11}H_{12}N_2O)_3Fe(SCN)_3$. This is readily soluble in alcohol, chloroform, and benzene, sparingly in water and ether.

Phenyltrimethylpyrazolone mercurochloride of constant composition is only obtained when a moderately concentrated aqueous solution of antipyrine is poured into a solution of mercuric chloride. It

forms a white, flocculent precipitate, melts at 150° , is only slightly soluble in hot water, is decomposed by concentrated acids, and gives a yellow precipitate of mercuric oxide with alkalis. With sodium peroxide, it yields metallic mercury. J. J. S.

Synthesis of Trimethylpyrazine and of Tetramethylpyrazine. By P. BRANDES and CARL STOEHR (*J. pr. Chem.*, 1896, [2], 53, 501—512; compare Abstr., 1895, i, 569).—Tri- and tetra-methylpyrazine are formed when dimethylpyrazine methobromide is heated in a sealed tube at 270 — 280° for six hours; the product is fractionated, and the fractions are purified by conversion into their mercuriochlorides. *Trimethylpyrazine*, $C_7H_{10}N_2$, is a colourless, highly refractive liquid; it does not solidify at 0° , and dissolves in water in every proportion, heat being developed; it boils at 171 — 172° (735 mm.), and is volatile in steam; its sp. gr. = 0.9958 at $0^{\circ}/4^{\circ}$ and 0.9787 at $18^{\circ}/4^{\circ}$. In most of its compounds it behaves as a monacid base. The *normal aurochloride*, $C_7H_{10}N_2 \cdot HAuCl_4 + H_2O$, melts at 72° , or when anhydrous at 110° ; it readily loses hydrochloric acid in water, passing into the *modified aurochloride*, $C_{10}H_7N_2 \cdot AuCl_3$, which melts at 137 — 138° . The *platinochlorides*, $(C_7H_{10}N_2)_2 \cdot HCl \cdot PtCl_4$, $C_7H_{10}N_2 \cdot H_2PtCl_6 + 2\frac{1}{2}H_2O$, and $C_7H_{10}N_2 \cdot PtCl_4$ are described. The *mercuriochloride*, $C_7H_{10}N_2 \cdot 5HgCl_2$, forms sparingly soluble, lustrous, white, prismatic needles. The *picrate*, $C_7H_{10}N_2 \cdot 2C_6H_3N_3O_7$, crystallises in lustrous, yellow, prismatic needles, and melts at 138 — 139° . The *methiodide*, $C_7H_{10}N_2 \cdot MeI$, crystallises in pale yellow, lustrous laminae, decomposes at 231° , and is unusually soluble in water; a *periodide* is described. The *methochloride*, together with its *aurochloride*,



(m. p. 145°), its *mercuriochloride*, $C_7H_{10}N_2 \cdot MeCl \cdot 6HgCl_2 + 2H_2O$ (m. p. 185°), its *platinochloride*, $C_7H_{10}N_2 \cdot Me_2PtCl_6$ were obtained. The base which Morin separated from fusel oil, and which boiled at 171 — 172° (Abstr., 1888, 572) was probably trimethylpyrazine.

Tetramethylpyrazine, $C_8H_{12}N_2$, has been described as dimethylketine (Abstr., 1881, 895), and has been obtained by Wolff (Abstr., 1887, 464) and Thal (Abstr., 1892, 1074); it crystallises in large, colourless, regular octahedra, melts at 86° , and boils at 189.5° (760 mm.). The *normal aurochloride*, $C_8H_{12}N_2 \cdot HAuCl_4 + 2H_2O$ (m. p. 173°), the *modified aurochloride*, $C_8H_{12}N_2 \cdot AuCl_3$ (m. p. 158°), the *picrate*, $C_8H_{12}N_2 \cdot 2C_6H_3N_3O_7$ (m. p. 191 — 192°), and the *mercuriochloride*, $C_8H_{12}N_2 \cdot 6HgCl_2$ (m. p. 155 — 165°), are described. A. G. B.

Derivatives of Phenylacetone. By ADALBERT KOLB (*Annalen*, 1896, 291, 253—297).—The action of ammonia on *o*-bromacetophenone having led to the production of diphenylpyrazine, the behaviour of bromophenylacetone towards the agent has been studied.

3 : 6-Diphenyldimethylpyrazine, $\begin{array}{c} CPh \cdot N \cdot CMe \\ | \quad | \\ CMe \cdot N \cdot CPh \end{array}$, is obtained by adding

bromine to a solution of phenylacetone in glacial acetic acid, heating the liquid until colourless, pouring it upon ice, and treating the bromophenylacetone thus precipitated with alcoholic ammonia during

8—14 days; the alcohol is then removed by distillation, and the residue, after dilution with water, is extracted with ether and hydrochloric acid. Dimethyldiphenylpyrazine is deposited by the ether, and crystallises from ethylic acetate in small, colourless prisms; it sublimes very readily, and melts at 126° . The substance is also formed on reducing phenylacetoxime with tin and hydrochloric acid, and treating with soda the hydrochloride of the amido-ketone thus produced; the dioxime obtained by the action of hydroxylamine on phenylacetoxime yields the same product. The hydrochloric acid extract, to which reference has been made, contains the base $C_{32}H_{36}N_6$, which crystallises from alcohol in needles, and melts at 225° ; the *hydrochloride* melts at 234 — 235° , the *sulphate* crystallises in needles, the *picrate* melts at 165 — 166° , and the *chromate* crystallises in small, red needles. The *mercurochloride* crystallises in needles, and the *platinochloride* forms reddish-yellow, rhombic prisms, blackens at 220° , and melts at 228° ; the *aurochloride* separates in rhombic crystals, and melts at 165 — 166° .

The alcoholic mother liquor of diphenyldimethylpyrazine deposits a mixture of two bases, which may be separated by means of their different solubility in benzene. The more sparingly soluble base, C_9H_9NO , crystallises from benzene in plates, and melts at 89 — 90° ; its *platinochloride* crystallises in yellow, quadratic leaflets. 3 : 6-

Diphenyldimethyldihydropyrazine, $\begin{array}{c} \text{CPh} \cdot \text{NH} \cdot \text{CMe} \\ | \qquad \qquad | \\ \text{CMe} \cdot \text{NH} \cdot \text{CPh} \end{array}$, is the base which dissolves more readily in benzene, and crystallises from alcohol in yellowish plates melting at 102° ; the *hydrochloride* crystallises in silky needles, and melts at 104 — 106° , solidifying at the latter temperature, and melting finally at 180 — 186° . The *mercurochloride* crystallises from water in long needles, and the *platinochloride* separates from alcohol in reddish-yellow, rhombic prisms; the *aurochloride* crystallises from alcohol in reddish-yellow needles, and melts at 144 — 145° .

Phenylacetoxime, $\text{NOH} \cdot \text{CPh} \cdot \text{COMe}$, is prepared by slowly adding phenylacetone to a well-cooled mixture of amylic nitrite and alcoholic sodium ethoxide, and extracting the liquid repeatedly with ether; treatment of the aqueous solution of the sodium derivative with acetic acid precipitates the ketoxime, which crystallises from the glacial acid in needles, whilst the ethereal extract deposits a compound, $C_{34}H_{30}O_4$, which crystallises from alcohol in small needles, and melts and decomposes at 209° . The *acetyl* derivative of phenylacetoxime crystallises from dilute alcohol in plates, and melts at 61 — 62° ; the *benzyl* derivative, which dissolves very readily in all agents excepting petroleum, melts at 62° . As already stated, reduction of phenylacetoxime gives rise to an amido-ketone; the *hydrochloride*, $C_9H_{11}NO \cdot \text{HCl}$, sinters at 200° , and becomes red and melts at 208° . The aqueous solution reduces cold Fehling's solution, and also mercuric chloride in presence of caustic soda; treatment with hot caustic alkali liberates benzaldehyde and ammonia. The *platinochloride* crystallises in dark red, six-sided prisms, and melts and decomposes at 215° .

3 : 6-Diphenylpyrazinedicarboxylic acid, $\text{COOH} \cdot \text{C} \begin{smallmatrix} \text{CPh} \cdot \text{N} \\ \text{N} \cdot \text{CPh} \end{smallmatrix} \text{C} \cdot \text{OOH}$, is produced when diphenyldimethylpyrazine is treated during 20—24 hours with a boiling 2 per cent. solution of potassium permanganate; it is very readily soluble in alcohol, crystallises from hot water in beautiful needles, and melts at 190° . The *ammonium* and *potassium* salts are very soluble in water, and the *silver* salt crystallises in small white needles; the *ethylic* salt crystallises from dilute alcohol in small needles, and melts at 104° . When diphenylpyrazinedicarboxylic acid is heated with glacial acetic acid in sealed tubes at 150 — 180° , carbonic anhydride is eliminated, and Staedel's isindole is produced.

The action of hydroxylamine on phenylacetoxime gives rise to the dioxime $\text{C}_9\text{H}_{10}\text{N}_2\text{O}_2$, melting at 239 — 240° , which Müller and von Pechmann obtained from phenyl methyl diketone and hydroxylamine (Abstr., 1889, 1170); along with it is produced a compound, $\text{C}_{27}\text{H}_{27}\text{N}_3\text{O}_7$, which melts at 117 — 118° . The *benzyl* derivative of the dioxime dissolves with difficulty in petroleum, and melts at 155° ; the *dibenzyl* derivative crystallises from petroleum in large needles, and melts at 55 — 56° .
M. O. F.

Oxidation of Quinazoline Derivatives. By STEFAN NIEMEN-ROWSKI (Ber., 1896, 29, 1356—1361).—*Uramidobenzoylcarboxylic acid*,

$\text{COOH} \cdot \text{C}_6\text{H}_3 \begin{smallmatrix} \text{NH} \cdot \text{CO} \\ \text{CO} \cdot \text{NH} \end{smallmatrix}$ [$\text{COOH} : \text{NH} : \text{CO} = 1 : 3 : 4$], is prepared

by boiling methyluramidobenzoyl with potassium permanganate in alkaline solution; in acid solution, at the ordinary temperature, the yield is smaller. Methyluramidobenzoyl is very stable towards chromic anhydride in glacial acetic acid solution, and the portion attacked is completely oxidised to carbonic anhydride. The acid is practically insoluble, except in alkalis, aniline, &c.; it readily forms gummy, colloidal, yellow aggregates, decomposes at about 405° , and appears to contain $1.5\text{H}_2\text{O}$. The *ammonium* salt exhibits, in moderately dilute solution, an intense blue fluorescence; the *silver* salt is colourless and flocculent.

4'-Hydroxyquinazoline chromate, $\text{C}_8\text{H}_6\text{N}_2\text{O} \cdot \text{CrO}_3$, crystallises in pomegranate-coloured quadratic plates, chars at about 200° , and is extremely stable towards chromic anhydride. When oxidised by means of chromic anhydride, 4'-hydroxyquinazoline yields ortho-uramidobenzoyl, $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{NH} \cdot \text{CO} \\ \text{CO} \cdot \text{NH} \end{smallmatrix}$, in very small quantity.

2'-Methyl-4'-hydroxyquinazoline hydrochloride, $\text{C}_9\text{H}_8\text{N}_2\text{O} \cdot \text{HCl}$, crystallises in colourless plates or slender needles, and decomposes at 336° ; the *nitrate* crystallises in colourless needles melting at 195° ; the *chromate* forms yellow, nodular masses, decomposes suddenly at 182° , and becomes dark brown when exposed to direct sunlight. The base is not oxidised by boiling nitric acid; potassium permanganate in alkaline solution attacks only a small portion, which is converted into carbonic anhydride.
J. B. T.

Phthalazine Derivatives. By OTTO BROMBERG (*Ber.*, 1896, **29**, 1434—1442; compare Gabriel and Neumann, *Abstr.*, 1893, i, 346).—The best method of preparing benzylphthalazone is to heat benzylidene phthalide and hydrazine with dilute alcohol in sealed tubes at 100°; the yield is quantitative.

1':3'-*Benzylmethylphthalazone*, $C_6H_4 < \begin{smallmatrix} C(C_7H_7) \\ CO \cdot NMe \end{smallmatrix} > N$, is formed when benzylphthalazone, dissolved in dilute alcohol, is mixed with excess of methylic iodide; it is insoluble in water and hydrochloric acid, and crystallises from methylic or ethylic alcohol in shining crystals melting at 148°. 1:3-*Benzylethylphthalazone*, $C_{17}H_{16}ON_2$, crystallises from methylic alcohol in white crystals, which become yellow on exposure to air; it is insoluble in hydrochloric acid, and melts at 106°.

1-*Benzylphthalimidine*, $C_6H_4 < \begin{smallmatrix} CH(C_7H_7) \\ CO \end{smallmatrix} > NH$, obtained on reducing 1-benzylphthalazone by means of zinc and acetic acid, forms stellate groups of needles, melts at 137°, and dissolves readily in alcohol, benzene, acetic acid, and strong hydrochloric acid. When warmed with phosphorus oxychloride, it gives a carmine red solution. It appears to be identical with the substance obtained on reducing benzylphthalimide with hydriodic acid.

4':1'-*Ethoxybenzylphthalazine*, $C_6H_4 < \begin{smallmatrix} C(C_7H_7):N \\ C(OEt):N \end{smallmatrix} >$, formed by acting on benzylchlorophthalazine with sodium ethoxide, dissolves readily in nearly all the ordinary solvents, but is sparingly soluble in water, and is practically insoluble in petroleum; it is deposited from alcohol in crystals, and melts at 84—86°. 4':1'-*Phenoxybenzylphthalazine*, $C_{21}H_{16}ON_2$, produced by a similar reaction, crystallises from alcohol in cube-like crystals, and melts at 155°; its solution in hydrochloric acid gives a precipitate with platinum chloride. Attempts to produce derivatives of isoindole and dihydroisoindole by reducing benzylchlorophthalazine proved unsuccessful.

Propylidenephthalide, $CO < \begin{smallmatrix} C_6H_4 \\ O \end{smallmatrix} > C:CHEt$, is prepared by heating phthalic and butyric anhydrides with sodium butyrate at 175° during eight hours; it forms a viscid, clear yellow oil, which solidifies to a mass of slender, white needles in a freezing mixture, but regains its fluidity at ordinary temperatures; it boils at 169—170° under 12 mm. pressure. It dissolves in potash, subsequent addition of hydrochloric acid causing the precipitation of *butyrophenoneorthocarboxylic acid*, $COPr^a \cdot C_6H_4 \cdot COOH$; the latter dissolves in ether and ethylic acetate, and crystallises from a mixture of ethylic acetate and petroleum in groups of colourless needles melting at 89°.

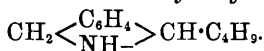
Propylidinephthalide and hydrazine unite in alkaline solution, with production of 1-*propylphthalazone*, $C_6H_4 < \begin{smallmatrix} CPr^a:N \\ CO-NH \end{smallmatrix} >$; the latter is insoluble in water, but dissolves in hydrochloric acid, and crystallises from alcohol in long, colourless needles, melting at 156°. 1'-*Propylphthalimidine*, $C_6H_4 < \begin{smallmatrix} CHPr^a \\ CO \end{smallmatrix} > NH$, is produced by the reduction of

the foregoing substance; it crystallises from hot water in white needles, melting at 135—136°, and is soluble in ether.

4':1'-Chloropropylphthalazine, $C_6H_4 < \begin{smallmatrix} CPr^a:N \\ CCl:N \end{smallmatrix} >$, is readily prepared by acting on propylphthalazone with phosphorus oxychloride at 100°; it crystallises from dilute alcohol in colourless needles melting at 67°. It dissolves readily in warm dilute hydrochloric acid, and the resulting solution yields precipitates on addition of platinum and gold chlorides, potassium ferrocyanide, and dichromate. When reduced by means of zinc and hydrochloric acid, it yields a base which proves to be 1'-propyldihydroisoindeole, $C_6H_4 < \begin{smallmatrix} CPr^a \\ CH_2 \end{smallmatrix} > NH$; this decomposes on exposure to air, and has an odour resembling piperidine. The hydrochloride, $C_{11}H_{13}N \cdot HCl$, melts at 203°; its solution gives precipitates with platinum and gold chlorides, picric acid and potassium ferrocyanide, but not with potassium chromate.

Isobutylidenephthalide, $CO < \begin{smallmatrix} C_6H_4 \\ O \end{smallmatrix} > C:C_4H_9$, is prepared by heating isovaleric anhydride, phthalic anhydride, and sodium isovalerate at 220° during five hours. It forms large crystals, and dissolves readily in hot alkalis and all the ordinary solvents with the exception of light petroleum. It crystallises from benzene or amyl alcohol in light yellow, isolated crystals, which melt at 97°. Isovalerophenone-orthocarboxylic acid, $C_4H_9 \cdot CO \cdot C_6H_4 \cdot COOH$, is obtained in the form of its potassium salt when the foregoing substance is heated with aqueous potash; it crystallises from a mixture of ethyl acetate and light petroleum in needles, and, when dried, melts at 88°.

1'-Isobutylphthalazone, $C_6H_4 < \begin{smallmatrix} C(C_4H_9) \\ CO-NH \end{smallmatrix} > N$, crystallises from alcohol in white crystals, and, when dried at 100°, melts at 113°. 4':1'-Chlorisobutylphthalazine, prepared from the latter by the action of phosphorus oxychloride, forms a clear syrup, which dissolves in hydrochloric acid without giving a crystalline hydrochloride; it affords, however, a crystalline picrate, $C_{12}H_{13}N_2Cl \cdot C_6H_3N_3O_7$, and a platinochloride, $(C_{12}H_{13}N_2Cl) \cdot H_2PtCl_6$, the former being a bright yellow substance which crystallises from alcohol, and melts at 122°, the latter melting at 216°. The foregoing base, when reduced by zinc and hydrochloric acid, yields another, which is oily and does not give crystalline salts; the platinochloride, however, is crystalline, and on analysis proves to have the composition $(C_{12}H_{17}N)_2 \cdot H_2PtCl_6$, and is therefore probably derived from isobutyldihydroisoindeole,



A. L.

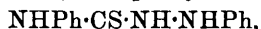
Constitution of Safranines. By RUDOLF NIETZKI (*Ber.*, 1896, 29, 1442—1446).—The author objects to some of the conclusions of O. Fischer and Hepp (this vol., i, 323), and to the nomenclature proposed by Jaubert (*ibid.*, 325). He has obtained the same mauveïne from metamidodiphenylamine and paramidodiphenylamine, and from diphenylmetaphenylenediamine and paraphenylenediamine; had the condensation taken place unsymmetrically, different substances would

have been obtained, so it is inferred that the safranines have symmetrical formulæ.

The azonium formula is to be preferred to the quinoneimide one, on account of the marked basic character of the safranines; diacetyl-safranine, for example, in spite of its two acetyl groups, is still a strong base.

C. F. B.

Action of Nitrous acid on Diphenylthiosemicarbazide and Diphenylsemicarbazide. By MAX BUSCH and JULIUS BECKER (*Ber.*, 1896, 29, 1686—1691).—Diphenylthiosemicarbazide,



is readily prepared by heating phenylthiocarbazonic acid with aniline, hydrogen sulphide being eliminated; the reaction appears to be a general one for primary and secondary amines. By the action of nitrous acid the carbazide probably yields a nitroso-derivative, $\text{NO}\cdot\text{NPh}\cdot\text{CS}\cdot\text{NH}\cdot\text{NPh}$, which changes spontaneously into the cyclic compound,

$\begin{array}{c} \text{NPh}\cdot\text{N} \\ | \quad | \\ \text{CS}-\text{N} \end{array} > \text{NPh}$; by the further action of nitrous acid, sulphur is eliminated, the compound being oxidised to 1 : 3-diphenyl-isotetrazolone,



with Bladin's tetrazole, $\text{CH} < \begin{array}{c} \text{N}-\text{N} \\ || \\ \text{NH}\cdot\text{N} \end{array}$, and resembles in constitution

Zincke's pseudoazimido-derivatives, $\begin{array}{c} \text{C}\cdot\text{N} \\ | \quad | \\ \text{C}\cdot\text{N} \end{array} > \text{NR}$. It crystallises in

dark red needles, melts and decomposes at 110° , and, in acid solution, dyes silk golden orange, the colour being stable. The yield is quantitative, and the molecular weight, determined by the cryoscopic method in phenolic solution, agrees with the formula. The salts are yellow and stable in presence of free acid at the ordinary temperature, but when boiled, they yield phenylazocarbonanilide (see below). The isotetrazolones are not changed by alkalis; they differ from the tetrazolones in colour and basicity. The *hydrochloride* crystallises in lemon coloured needles melting at 164° ; the *sulphate*, $\text{C}_{13}\text{H}_{10}\text{ON}_4\cdot\text{H}_2\text{SO}_4$, *picrate*, and *platinochloride*, $\text{C}_{13}\text{H}_{10}\text{ON}_4\cdot\text{H}_2\text{PtCl}_6$, crystallise in yellow needles melting at 188° , $133\text{--}134^\circ$, and 218° respectively; the *nitrate* also crystallises in slender, golden needles. Diphenylsemicarbazide is formed by the reduction of the isotetrazolone by means of zinc dust and acetic acid, showing that the phenyl group retains its original position.

Nitrosodiphenylsemicarbazide, $\text{NO}\cdot\text{NPh}\cdot\text{CO}\cdot\text{NH}\cdot\text{NPh}$, prepared from diphenylsemicarbazide and nitrous acid, crystallises in slender needles, melts at $174\text{--}175^\circ$, quickly decomposes in moist air, and gives Liebermann's reaction. When warmed with alcohol, phenylazocarbonanilide is formed, and all attempts to prepare the diphenyl-isotetrazolone were unsuccessful.

Phenylazocarbonanilide, $\text{NPh}\cdot\text{N}\cdot\text{CO}\cdot\text{NHPh}$, prepared in the manner described above, is also formed when diphenylsemicarbazide is oxidised by means of ferric chloride; it crystallises in lustrous,

orange-red plates, melts at $121-122^{\circ}$, gives no nitroso-derivative, and is not changed by acids or alkali.

J. B. T.

Ketones of the Tropine Group. III. Tropinone and Nortropinone. By RICHARD WILLSTÄTTER (*Ber.*, 1896, **29**, 1575—1584; compare this vol., 327).—When tropinone hydrochloride is treated with potassium cyanide in aqueous solution, *tropinonecyanhydrin*, $C_9H_{14}N_2$, is formed. It crystallises in long, colourless, lustrous prisms, and melts and decomposes into its constituents at 145° . *α-Ecgonine* is formed by the hydrolysis of this compound, and is a very hygroscopic neutral substance. It will shortly be more fully described.

Tropigenine can readily be purified by recrystallisation from ether followed by conversion into the *carbamate*, which melts and decomposes at 166° . *n-Benzoyltropigenine*, $C_7H_{12}ONBz$, crystallises in milk-white aggregates of slender prisms, and melts at 125° . It is less soluble in water at $50-60^{\circ}$ than in either cold or boiling water. When tropigenine carbamate is treated with chromic acid, it is converted into *nortropinone*, $C_7H_{11}NO$, which crystallises in thin, colourless needles and plates, melting at $69-70^{\circ}$. This substance closely resembles tropinone in its properties. The *carbamate* is a snow-white, hygroscopic mass. The *hydrochloride* is very hygroscopic, and melts and decomposes at 201° . The *platinochloride* decomposes above 200° , the *aurochloride* melts and decomposes at 168° , and the *picrate* melts at $158-160^{\circ}$.

Nitrosonortropinone crystallises in yellowish needles, melts indefinitely at about 127° , and shows Liebermann's reaction faintly. *Nortropinonoxime*, $C_7H_{11}N:NOH$, is sparingly soluble in cold water, crystallises in thin, rhomboidal plates, and melts at $181-182^{\circ}$. *n-Benzoylnortropinonoxime*, $C_7H_{10}NBz:NOH$, melts at 175° .

A. H.

Bases from the Cell-nucleus. By ALBRECHT C. L. M. L. KOSSEL (*Zeit. physiol. Chem.*, 1896, **22**, 176—187).—Protamine is a substance originally prepared by Miescher from the spermatozoa of the salmon. Piccard attributed to it the formula $C_{16}H_{31}N_9O_4$.

In the present research it was prepared both from salmon and sturgeon sperm. The sulphate from salmon sperm has the formula $C_{16}H_{31}N_9O_3 \cdot H_2SO_4$. That from sturgeon sperm has rather different solubilities in sodium chloride solutions, and the names *salmine* and *sturine* are suggested by the two protamines. By decomposing the latter base with sulphuric acid, a new crystalline base was prepared, which is called *histidine*; its *hydrochloride*, which forms large, colourless, rhombic crystals [$a : b : c = 0.76665 : 1 : 1.71104$], has the formula $C_{12}H_{20}N_6O_4 \cdot 2HCl + 2H_2O$ or $C_6H_9N_3O_2 \cdot HCl + H_2O$. Among the other decomposition products, arginine was obtained, but little or no amino-acids. The protamines give the biuret, but not Millon's, reaction.

W. D. H.

Formation of Ethylic Cholate. By LASSAR COHN (*Zeit. physiol. Chem.*, 1896, **22**, 196).—The author now confirms Vahlen's statement (this vol., i, 453) that ethylic cholate is not formed when pure cholic

acid is boiled with alcohol. The impure acid employed in his earlier observations contained hydrochloric acid, which acted as an etherifying agent.

Behaviour of Paracasein with Rennet. By OLOF HAMMARSTEN (*Zeit. physiol. Chem.*, 1896, **22**, 103—126).—The term paracasein is used for casein which has been acted on by rennet; the term casein being used synonymously with caseinogen.

The statement originally made by the author and unanimously adopted that casein differs from caseinogen in that the latter is, whilst the former is not, curdled by rennin *plus* calcium salts has been recently questioned by Peters (*Preisschrift. Rostock*, 1894). Peters alleges that when casein is dissolved in lime water, and Witte's "Labessenz" added, a precipitation occurs. This is not, however, due to the action of the enzyme, but is produced by the large amount of sodium chloride present in the preparation used; the calcium compound of casein is very readily precipitated by sodium chloride, especially at 40°.

W. D. H.

Note by Abstractor.—Practically the same conclusion was arrived at by Edmunds (this vol., ii, 489), who, however, was unable to obtain Witte's preparation. He was inclined to attribute the action rather to calcium salts than to sodium salts in the essence.

W. D. H.

Optical Behaviour of some Vegetable Proteids. By JOHAN GUSTAV CHRISTOPHE THORSAGER KJELDAHL (*Bied. Centr.*, 1896, **25**, 197—199; from *Forhandl. skand. Naturfors.*, 1892, 385—390).—The amount of proteids extracted from wheat meal by dilute alcohol varies according to the strength of the alcohol (minimum with 20 per cent., maximum with 55 per cent., alcohol), but is not influenced by the amount of alcohol, by the length of time, and only slightly by the temperature. In the author's experiments 55 per cent. alcohol was employed at the ordinary temperature. The proteids were precipitated by cooling with freezing mixtures, being several times redissolved and precipitated by cooling. Finally they were precipitated with a large amount of absolute alcohol, treated with ether, and dried in a vacuum. All the preparations showed an almost constant percentage of carbon (about 52.0 per cent.) and nitrogen (17.25 per cent.), and a rotatory power, in 55 per cent. alcohol, of $[\alpha]_D = -92^\circ$. Ritthausen supposed that wheat meal contains three proteids soluble in alcohol, but the above results indicate the presence of only one.

The rotatory power of acetic acid solutions depends on the strength of the acid. With glacial acid $[\alpha]_D = -81^\circ$; with 5 to 0.1 per cent. $[\alpha]_D = -111^\circ$. Solutions in very dilute caustic alkali solutions gave the same result as dilute acetic acid. With solution in phenol at 40° $[\alpha]_D = -130^\circ$.

The solubility of the proteids of rye meal resembled that of wheat meal. C = 53.6, N = 17.20 per cent. $[\alpha]_D$ in 55 per cent. alcohol = -121° , in dilute acids = -144° , in glacial acetic acid = -105° , and in phenol = -157° .

The proteids of barley meal again showed similar solubility.

C = 53.0, N = 16.52 per cent. The rotatory power of the different solutions was less constant than in the case of wheat and rye. The average results were: In 55 per cent. alcohol $[\alpha]_D = -111^\circ$, in dilute acetic acid = -130° , and in phenol = -149° .

In the case of oat meal, the greatest solubility was in 60 per cent. alcohol, which, however, did not dissolve much, and the soluble compound readily changes to an insoluble modification. Alcoholic solutions could not be got clear enough for polarisation. In dilute acetic acid or caustic soda $[\alpha]_D = -83^\circ$ (?).

With maize meal, the minimum solubility was with 40 to 50 per cent., the maximum with 75 to 85 per cent., alcohol; and the proteïds have to be precipitated with water. $[\alpha]_D = -35^\circ$ in 75 per cent. alcohol and -28° in glacial acetic acid. Dilute acetic acid solutions are completely precipitated by sodium chloride. On the other hand, the solvent power of dilute alcohol is increased by addition of sodium or calcium chlorides, and the rotatory power seems to be slightly raised by such addition.

N. H. J. M.

Colour Reactions of Proteïds with Nitrous acid and Phenols. By KARL LANDSTEINER (*Chem. Centr.*, 1895, ii, 891; from *Centr. Physiol.*, 9, 433—434; compare this vol., ii, 284).—The author shows that his former statement that no diazo-compound results from the action of nitrous acid on proteïds is incorrect.

The compound obtained on treating salicylic acid with nitrous acid is a *diazosalicylic acid*, $C_7H_4O_3N_2$, which, when warmed with hydriodic acid, yields a colourless, crystalline, iodine compound. From a solution of sodium salicylate, which had been treated with sodium nitrite and hydrochloric acid, the author obtained a small quantity of a substance crystallising in needles; its reactions with brucine and diphenylamine proved it to be a nitrate, and the results of analysis agreed roughly with those required for diazophenol nitrate.

J. J. S.

Compounds of the Colouring Matter of the Blood with Heavy Metals. By JOAN JUTT (*Chem. Centr.*, 1895, ii, 683; from *Pharm. Zeit. Russ.*, 34, 503—505).—Oxyhæmoglobin obtained from any particular species of animal, is a well-defined compound; that obtained from horse's blood has the composition C = 54.5, H = 7.25, N = 17.51, S = 0.449, F = 0.393, and O = 19.85 per cent., corresponding with the formula $C_{648}H_{1046}N_{178}S_2FO_{177}$.

Oxyhæmoglobin readily forms compounds with salts and double salts of the heavy metals; the compounds thus obtained are very sparingly soluble in blood, especially in the presence of sodium chloride. On this basis, the author has constructed a method for the volumetric estimation of the colouring matter in blood by means of zinc and copper salts. The metallic compounds are obtained by the replacement of five hydrogen atoms in oxyhæmoglobin by five atoms of a metal, the valency of the metal appearing to be without influence. The main action of heavy metals as poisons is that the formation of the metallic compounds with the oxyhæmoglobin renders the blood incapable of acting as an oxygen carrier.

J. J. S.

Organic Chemistry.

Preparation of Cyanogen Bromide, Bromonitromethane, and Dibromonitromethane. By ROLAND SCHOLL (*Ber.*, 1896, **29**, 1822—1825).—In order to avoid the separation of insoluble by-products on adding bromine to a concentrated solution of potassium cyanide, the author has modified the preparation of cyanogen bromide in the following manner. A solution of 65 grams of potassium cyanide in 120 grams of water, cooled to 0°, is slowly added to 150 grams of bromine, maintained at the temperature of melting ice, the liquid being agitated during the operation; the yellow product is heated at 65—70° in a retort, when 90 per cent. of the calculated amount of cyanogen bromide distils over. The crystalline substance which separates during the action, is probably a double compound of potassium bromide and cyanogen bromide; it is decomposed at the temperature subsequently attained.

Tscherniak's method of preparing mono- or dibromonitromethane consists in adding an aqueous solution of the sodium derivative of nitro- or bromonitro-methane to the calculated quantity of bromine. By excluding water, however, the author has succeeded in considerably improving the yield of these substances; the sodium derivative is added to the theoretical amount of bromine dissolved in carbon bisulphide, sodium bromide being then removed by agitation with water, and excess of the halogen by treatment with sulphurous acid.

M. O. F.

Action of Acetylene on Iron, Nickel, and Cobalt reduced by Hydrogen. By HENRI MOISSAN and CHARLES MOUREU (*Compt. rend.*, 1896, **122**, 1240—1243).—Acetylene acts readily at the ordinary temperature on iron, nickel, and cobalt if they have been reduced from their oxides at the lowest possible temperature. There is great development of heat, and, if the current of gas is rapid, the metal becomes incandescent. Part of the acetylene is converted into benzene and other polymerides, but the greater part splits up into carbon and hydrogen.

It would seem that the phenomena are due to the energetic absorption of the gas by the porous reduced metal; heat is thus developed, part of the acetylene is polymerised, and part is decomposed. As soon as decomposition begins, the reserve energy of the acetylene becomes available and contributes to the energy of the reaction. Carefully prepared spongy platinum produces a similar decomposition. On the other hand, if the acetylene is diluted with nitrogen, there is no incandescence, though the acetylene is absorbed and slightly decomposed.

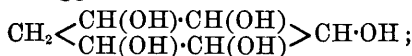
If the metals have been heated at too high a temperature during the process of reduction, heat is necessary in order to start the decomposition of the acetylene.

C. H. B.

Preparation of Methylic Nitrate. By MARCEL DELÉPINE (*Bull. Soc. Chim.*, 1895, [3], 13, 1044—1045).—The author recommends the following modified form of Champion's method for the preparation of methylic nitrate: 50 c.c. of concentrated sulphuric acid are slowly added to 150 c.c. of methylic alcohol (98—99 per cent.), care being taken that the temperature does not rise too much. This mixture is then gradually poured into a previously prepared mixture of 100 c.c. of concentrated sulphuric acid and 150 c.c. of pure nitric acid (36°), which is kept at a temperature of 12—14°. 100 c.c. of concentrated sulphuric acid is then added, and the whole quickly agitated by means of a glass ring; the temperature rises to 20°, and in a few minutes all the ethereal salt separates. The yield is good.

J. J. S.

Quercitol. By HEINRICH KILIANI and J. SCHÄFER (*Ber.*, 1896, 29, 1762—1766).—The molecular refractive power of quercitol, and the production of benzene when it is reduced by means of hydriodic acid, led Kanonnikoff to suggest that its formula is



if this is correct, it should yield malonic acid when oxidised by means of potassium permanganate; this is found to be the case. The quercitol (1 part) is dissolved in water (100 parts) and mixed at the ordinary temperature with potassium permanganate (4 parts), dissolved in water (120 parts). The malonic acid was identified by means of the calcium and barium salts. In addition to malonic acid, the oxidation products are oxalic acid, carbonic anhydride, an acid, in very small quantity, probably isomeric with malic acid, and, in considerable quantity, a compound which readily reduces alkaline copper solution. These results prove that quercitol contains a CH_2 group, which, by the action of concentrated nitric acid, is attacked in two ways, since Kiliani and Scheibler have previously shown, that in these circumstances it yields mucic acid and trihydroxyglutaric acid.

By the action of bromine water on quercitol, a diketone, $\text{C}_6\text{H}_8\text{O}_5$, is probably formed, but its separation from bromo-derivatives, which are simultaneously produced, is extremely difficult; at the ordinary temperature it yields an *osazone*, $\text{C}_{18}\text{H}_{20}\text{O}_5\text{N}_4$, crystallising in yellow or yellowish-red aggregates of needles, softening at 170°, and melting and decomposing at about 180°.

The removal of the excess of bromine and of hydrogen bromide in cases such as the above, where bromine water has been employed as an oxidising agent, is conveniently accomplished by shaking the liquid with successive portions of silver oxide; this is more convenient than passing a current of carbonic anhydride through the liquid and heating it.

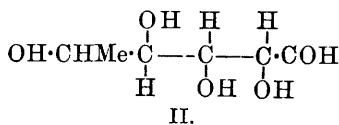
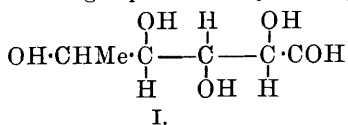
J. B. T.

Ammoniacal Derivatives of Mannose, of Sorbose, and of Galactose. By CORNELIS A. LOBRY DE BRUYN, and FREDERICK H. VAN LEENT (*Rec. Trav. Chim.*, 1896, 15, 81—83; compare *Abstr.*, 1896, i, 118).—When an ammoniacal solution of mannose in methylic alcohol is evaporated in a vacuum and then treated with a little dry

ether, an amorphous substance, which gradually becomes crystalline, separates; this melts and decomposes at about 158° , and has the composition $C_{12}H_{23}O_{10}N$, being formed from 2 mols. of mannose and 1 mol. of ammonia by the loss of 1 mol. of water. Its specific rotatory power, $[\alpha]_D = -28.3^{\circ}$, and, when boiled with an acid and then neutralised with alkali, it yields mannose.

Sorbosamine, $C_6H_{13}NO_4$, was obtained by treating an ammoniacal solution of sorbose in methylic alcohol which had been evaporated in a vacuum, with dry ether. The quantity obtained was too small to be completely investigated. When galactosamine (*loc. cit.*) is boiled with absolute methylic alcohol, and ether is added, a hygroscopic crystalline deposit is formed having the same composition as the above-mentioned ammoniacal derivative of mannose; it is formed by the elimination of a molecule of ammonia from 2 mols. of glucosamine. J. J. S.

Isorhamnose. By EMIL FISCHER and HEINRICH HERBORN (*Ber.*, 1896, 29, 1961—1967).—The well-known method of inducing intramolecular change in acids of the sugar group by means of hot pyridine, has been applied to rhammonic acid, which is thus converted into isorhammonic acid; reduction of the lactone with sodium amalgam gives rise to isorhamnose, which has the configuration I, rhamnose being represented by the expression II.



Rhammonic acid is prepared by oxidising rhamnose with bromine water; the lactone dissolves in acetone with some difficulty, 100 parts being required for 3.85 parts of the substance at 20° . The *brucine* salt dissolves in three parts of boiling alcohol, and crystallises in long, colourless needles; it sinters at 120° , and melts at 126° .

Isorhammonic acid, $\text{OH} \cdot \text{CHMe} \cdot \text{C}(\text{OH})(\text{H}) - \text{C}(\text{OH})(\text{H}) - \text{C}(\text{OH})(\text{H}) \cdot \text{COOH}$, is obtained by

dissolving 200 grams of rhamnolactone in 1 litre of water, and heating it in autoclaves with 170 grams of pyridine for three hours at 150 — 155° ; it is separated from the product by means of the *brucine* salt, which crystallises in lustrous needles, and melts at 165° . The *lactone* separates from ethylic acetate in colourless crystals, and melts at 150 — 152° , becoming brown at 190 — 200° ; it dissolves very readily in water, and, being in part converted into the acid, exhibits very rapid alteration of specific rotatory power, which falls from -62.02° to -46° in 20 minutes, and becomes constant at -5.21° if heated during 24 hours. The *phenylhydrazide* crystallises from alcohol in slender needles, and dissolves with difficulty in acetone; it sinters at 148° , and melts at 152° .

When isorhamnolactone is oxidised with dilute nitric acid, inactive xylotrihydroxyglutaric acid is formed, identical with the substance

obtained from xylose (Fischer and Piloty, *Abstr.*, 1892, i, 440); rhamnose and rhammonic acid, when oxidised in this manner, yield the lævorotatory acid.

Isorhamnose is obtained by reducing the lactone with 2½ per cent. sodium amalgam. The *phenylhydrazone* is very readily soluble, and the osazone is identical with rhamnosazone; the *ethyl mercaptal* crystallises from ether, and melts at 97—98° (corr.). Boiling dilute hydrochloric acid converts isorhamnose into δ -methylfurfuraldehyde (compare Fischer and Liebermann, *Abstr.*, 1894, i, 4), and the sugar combines with hydrogen cyanide, forming the nitrile of a dicarboxylic acid.

M. O. F.

Transformation of Sugars by means of Lead Hydroxide.

By CORNELIS A. LOBRY DE BRUYN and W. ALBERDA VAN EKENSTEIN (*Rec. Trav. Chim.*, 1896, **15**, 92—96).—In consequence of the recent publication by Svobodo (this vol., i, 406) of his researches on the action of basic lead acetate solutions on different sugars, the authors are obliged to publish their work on the transformation of sugars by means of lead hydroxide. The products obtained by the action of this reagent differ somewhat from those formed by the action of potash, soda, or lime (this vol., i, 116). Glucose when heated with lead hydroxide yields mannose, but no fructose; fructose although transformed yields neither glucose nor mannose as it does with potash. Mannose, also, is not at all, or only very slightly, transformed into fructose.

A comparative table, showing the action of lead hydroxide and potash on glucose, mannose, fructose, and galactose, is given. This contains the specific rotatory power after transformation, the amount of the transformed material destroyed by boiling with hydrochloric acid and the specific rotatory power of the residue.

J. J. S.

New Hydrazones of Sugars. Naphthylhydrazones and Alkylated Phenylhydrazones. By W. ALBERDA VAN EKENSTEIN and CORNELIS A. LOBRY DE BRUYN (*Rec. Trav. Chim.*, 1896, **15**, 97—99).—The authors have prepared the unsymmetrical naphthylhydrazones, also the α -ethyl-, α -amyl-, α -allyl-, and α -benzyl-hydrazones of various sugars, namely glucose, galactose, mannose, arabinose, rhamnose, xylose, and lactose. Many of these hydrazones will, probably, be of use in separating mixtures of sugars, on account of their different solubilities, &c. Fructose yields no crystalline compound with any of the hydrazines mentioned.

A detailed account of the properties of these hydrazones will shortly appear.

J. J. S.

Methylamines. By MARCEL DELÉPINE (*Compt. rend.*, 1896, **122**, 1272—1274; compare this vol., i, 519).—Methylamine hydrochloride melts indistinctly at about 210°, dimethylamine hydrochloride forms long prisms which melt sharply at 171°, and trimethylamine hydrochloride melts at about 271—275°, a temperature much higher than that stated by Cambier and Brochet.

The picrates of the methylamines, unlike the hydrochlorides, are

only slightly soluble, are not deliquescent, and have somewhat well defined melting points. The salts of methylamine and dimethylamine can be obtained by the direct action of picric acid on the methylic compounds previously described (*loc. cit.*). *Methylamine picrate* forms large rhombic crystals which melt at 207° (uncorr.) and dissolve in 75 parts of water at 11° ; *dimethylamine picrate* forms flattened rhombic crystals which melt at $155\text{--}156^{\circ}$ (uncorr.) and dissolve in 56 parts of water at 11° ; *trimethylamine picrate* crystallises in small needles which melt at 216° (uncorr.), and dissolve in 77 parts of water at 11° . The methylamine salt is orange-yellow, the trimethylamine salt lemon-yellow, whilst the colour of the dimethylamine salt is intermediate.

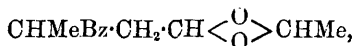
With iodine in presence of an alkali, trimethylamine readily yields the compound Me_3NI_2 which melts at 66° , whilst a solution of iodine in an alkali iodide added to a salt of trimethylamine gives a green crystalline precipitate of the compound $\text{Me}_3\text{NI}\cdot\text{HI}$, already described by Weiss; it melts at 65° . The other two amines give no similar precipitate.

Nessler's reagent with di- and trimethylamine gives a white precipitate, soluble in water, but with methylamine it forms a pale yellow precipitate insoluble in water or an excess of the reagent. It has the composition $\text{Me}_2\text{N}_2\cdot 3\text{HgI}_2\cdot \frac{1}{2}\text{Hg} + \text{H}_2\text{O}$. C. H. B.

The Reaction of Triethylphosphine with Oxygen. By W. P. JORISSEN (*Ber.*, 1896, 29, 1707—1709).—When triethylphosphine is exposed to air in the absence of water, it always absorbs rather more oxygen than is necessary for the formation of triethylphosphine oxide, POEt_3 , a small amount of the ethereal salt of phosphinic acid being also formed. In the presence of water, on the other hand, the amount of oxygen is exactly that calculated for the formation of the oxide. When the absorption takes place in the presence of a substance such as indigo, which is not attacked by ordinary oxygen, the colouring matter is rapidly oxidised, and the absorption of oxygen is exactly doubled. A. H.

Action of Sodium on Acetaldehyde. By PAUL C. FREER (*Amer. Chem. J.*, 1896, 18, 552—562).—Acetaldehyde reacts violently with sodium so that dilution with ether and cooling are imperative; hydrogen is evolved and a white crystalline sodium compound, believed to be $\text{CH}_2\text{:CH}\cdot\text{ONa}$, separates, but polymerises to a brown substance before it can be analysed. When a mixture of benzoic chloride and aldehyde is run into a flask containing sodium covered by ether, hydrogen is evolved and sodium chloride separates; if the ethereal solution is washed with water and dilute potash, to remove benzoic acid, dried over sodium sulphate, and evaporated in a vacuum, the residual oil yields white crystals. This compound has the formula $\text{C}_{13}\text{H}_{16}\text{O}_4$, melts at $86\text{--}87^{\circ}$, and dissolves in alcohol, benzene, and chloroform, but not in water. When heated with water at 100° , it yields benzoic acid, aldol, and aldehyde; when destructively distilled, or heated with dilute hydrochloric acid, it is converted into benzoic acid, crotonaldehyde, and acetaldehyde; when

warmed with alkalis it dissolves, and aldehyde resin is formed. From the behaviour of the compound as described above, the author concludes that the substance is *aldehydoaldol benzoate*,



sodium acetaldehyde being first formed during the preparation, and then undergoing condensation which stops at aldol if benzoic chloride is present, but otherwise proceeds further.

The mother liquor of the aldehydoaldol benzoate proved to be aldol benzoate, for it behaved on distillation identically with a similar syrup prepared from aldol, sodium, and benzoic chloride.

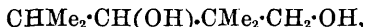
A. G. B.

Condensation Products of Isobutaldehyde. By G. URBAIN (*Bull. Soc. Chim.*, 1895, [3], 13, 1048—1052).—If isobutaldehyde is treated with its own weight of a 5 per cent. alcoholic solution of soda, a vigorous action takes place, and the product, after the evaporation of the alcohol, yields, on distillation at 15 mm. pressure, three fractions, (1) to 110°, (2) from 110—150°, (3) above 150°. The first fraction on further distillation at atmospheric pressure yields a compound boiling at 140°, and identical with that previously obtained by Fossek (*Abstr.*, 1882, 161) on heating the aldehyde with sodium acetate solutions in sealed tubes. Its composition is represented by the formula $\text{CMe}_2\text{CH} \cdot \text{CMe}_2 \cdot \text{CHO}$.

The second fraction yields a compound which boils at 125—130° under a pressure of 14 mm. This has the composition $\text{C}_8\text{H}_{16}\text{O}_2$, and is identical with Fossek's diisobutaldehyde (*loc. cit.*). Treated with acetic chloride it yields a *monacetyl* derivative which boils at 230—235°, and when reduced in ethereal solution with sodium it yields a crystalline compound, $\text{C}_8\text{H}_{18}\text{O}_2$, identical with the glycol, $\text{CHMe}_2 \cdot \text{CH}(\text{OH}) \cdot \text{CH}(\text{OH}) \cdot \text{CHMe}_2$, obtained by Fossek on treating isobutyraldehyde with alcoholic potash. Fossek's diisobutaldehyde is therefore *dimethyl-2:5-hexaneol-3-one-4*,



Its *oxime* boils at 133—135° under a pressure of 13 mm. The third fraction is still under investigation. If, when the soda is added to the isobutaldehyde, care is taken that no rise in temperature occurs and that the soda is neutralised by means of carbonic anhydride before evaporating off the alcohol, a colourless oil, which boils at 95° under a pressure of 14 mm. is obtained. This is *trimethyl-2:2:4-pentane-ol-3-al-1*, $\text{CHMe}_2 \cdot \text{CH}(\text{OH}) \cdot \text{CMe}_2 \cdot \text{CHO}$. The yield is poor as it is readily acted on by alkalis and converted into trimethylpenteneal and dimethylhexanediol. When treated with acetic anhydride in sealed tubes, it yields a *monacetyl* derivative which boils at 200—210°, and when reduced yields the glycol,



which forms a *diacetyl* derivative, boiling at 110—115°

J. J. S.

Hydrogenation of Pinacolone. By MAURICE DELACRE (*Compt. rend.*, 1896, **122**, 1202—1205).—The author considers that the general adoption of the formula, $\text{CMe}_3\cdot\text{COMe}$, for pinacolone, in preference to the formula, $\begin{matrix} \text{CMe}_2 \\ | \\ \text{CMe}_3 \end{matrix} > \text{O}$, is not supported by any decisive

evidence, and is to be traced (1) to the failure of all attempts to hydrogenise pinacolone and (2) to the analogies which must necessarily exist between the two functions represented by the formulæ, these analogies not yet having been clearly defined and differentiated.

Concentrated hydrobromic acid acts readily on pinacolone, and yields a compound of the composition $\text{C}_6\text{H}_{12}\text{Br}_2$. When heated with alcoholic potash, this product gives the same yield of the same hydrocarbon of the ethylene series as the pinacone bromide obtained by the same method. When reduced with zinc and acetic acid, both bromides give the same yield of tetramethylethylene. Further, pinacolone bromide, when heated in a sealed tube with alcoholic potash, yields no trace of acetylene. It follows that both pinacone and pinacolone bromides are symmetrical.

The other products of the action of hydrogen bromide on pinacolone and pinacone, are bipropenyl, very small quantities of pinacolone or an isomeride, and resinous products. With hydrochloric acid in place of hydrobromic acid, the quantity of the haloïd derivative obtained diminishes. With hydrochloric acid and pinacone, the yields are very similar to those obtained with hydrobromic acid and pinacolone; with hydrochloric acid and pinacolone, the latter simply dissolves and becomes brown, but no resinous products are formed.

It follows from these results that pinacolone can be hydrogenised indirectly; its exact constitution is still uncertain. C. H. B.

Action of Carbonyl Chloride on Dithioacetylacetone. By VICTOR VAILLANT (*Bull. Soc. Chim.*, 1895, [3], **13**, 1094—1095; compare *Abstr.*, 1895, i, 168).—A benzene solution of dithioacetylacetone, $\text{C}_{10}\text{H}_{14}\text{S}_2\text{O}_4$, was treated with an excess of carbonyl chloride, also dissolved in benzene, and the mixture kept for about two months; after evaporation, it yielded a small quantity of Thomas and Lefevre's dimethyldiacetylpyrone, $\text{CO} < \begin{matrix} \text{CAc}:\text{CMe} \\ \text{CAc}:\text{CMe} \end{matrix} > \text{O}$ (*Abstr.*, 1889, 235).

J. J. S.

Magnesium Nitride. By OSKAR EMMERLING (*Ber.*, 1896, **29**, 1635).—Magnesium nitride, although violently attacked by water, is not affected by acidyl chlorides or by alcohol and ethylic iodide at 200° . When, however, it is treated with cold acetic anhydride, heat is developed, and the product, when fractionally distilled, yields some quantity of an oil, boiling at $80\text{--}82^\circ$, which proves to be acetonitrile; in like manner, when treated with benzoic anhydride it yields benzonitrile. A. L.

New Derivatives of the Isomeric β -Chlorocrotonic acids. By WILHELM AUTENRIETH (*Ber.*, 1896, **29**, 1665—1670).—The acidyl chlorine atom of the isomeric β -chlorocrotonic chlorides is readily replaceable by amido-, acidyl-, and phenoxy-groups, and in all the

following instances the isomerism of the acids is represented in the compounds produced.

β -Chlorisocrotonic chloride distils without alteration, whilst β -chlorocrotonic chloride, under these conditions, undergoes complete isomeric change with production of the former compound.

β -Chlorisocrotonamide, $\text{Me}\cdot\overset{\text{H}}{\underset{\text{H}}{\text{C}}}\cdot\overset{\text{Cl}}{\text{C}}\cdot\text{CO}\cdot\text{NH}_2$, produced by the interaction of the corresponding chloride and aqueous ammonia, dissolves readily in alcohol, ether, chloroform, and hot water, and separates from the last two in pearly leaflets, melting at $109-110^\circ$. It is not altered by boiling with dilute mineral acids, but is partially decomposed by hot alkalis, hydrogen chloride being eliminated. It dissolves in 86 parts of water at 15° . β -Chlorocrotonamide, $\text{Cl}\cdot\overset{\text{H}}{\underset{\text{H}}{\text{C}}}\cdot\overset{\text{Me}}{\text{C}}\cdot\text{CO}\cdot\text{NH}_2$, dissolves readily in alcohol, ether, and chloroform; 22 parts of water at 15° dissolve 1 part of the amide. It crystallises from water in beautiful, transparent prisms or dull needles, and melts at $99-101^\circ$. When heated at $150-160^\circ$, it is carbonised.

β -Chlorisocrotonanilide, $\text{Me}\cdot\overset{\text{H}}{\underset{\text{H}}{\text{C}}}\cdot\overset{\text{Cl}}{\text{C}}\cdot\text{CO}\cdot\text{NHPh}$, is best prepared by the Baumann-Schotten reaction; it dissolves readily in alcohol and ether, but is insoluble in water; it crystallises from alcohol in flat, shining needles, and melts sharply at 106° ; it has feebly basic properties, being dissolved by concentrated hydrochloric acid and reprecipitated on addition of water. β -Chlorocrotonanilide, $\text{Cl}\cdot\overset{\text{H}}{\underset{\text{H}}{\text{C}}}\cdot\overset{\text{Me}}{\text{C}}\cdot\text{CO}\cdot\text{NHPh}$, is similar in properties to the isomeric anilide; it crystallises from alcohol in fine prisms and melts at $123-124^\circ$. β -Chlorisocrotonic- α -naphthylamide, $\text{Me}\cdot\overset{\text{H}}{\underset{\text{H}}{\text{C}}}\cdot\overset{\text{Cl}}{\text{C}}\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_{10}\text{H}_7$, is readily soluble in alcohol and ether, but is insoluble in water; it crystallises from alcohol in flat, shining needles, and melts at 155° . β -Chlorocrotonic- α -naphthylamide, $\text{Cl}\cdot\overset{\text{H}}{\underset{\text{H}}{\text{C}}}\cdot\overset{\text{Me}}{\text{C}}\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_{10}\text{H}_7$, crystallises from alcohol in fine prisms, and melts at $169-170^\circ$.

β -Naphthyllic β -isochlorocrotonate, $\text{Me}\cdot\overset{\text{H}}{\underset{\text{H}}{\text{C}}}\cdot\overset{\text{Cl}}{\text{C}}\cdot\text{COOC}_{10}\text{H}_7$, prepared by the action of the chloride on the sodium compound of β -naphthol, is insoluble in water, but dissolves readily in alcohol and ether; it crystallises from alcohol in white, shining leaflets, and melts at 67° . β -Naphthyllic β -chlorocrotonate, $\text{Cl}\cdot\overset{\text{H}}{\underset{\text{H}}{\text{C}}}\cdot\overset{\text{Me}}{\text{C}}\cdot\text{COOC}_{10}\text{H}_7$, separates from alcohol as an indistinctly crystalline mass, and melts at $99-100^\circ$.

A. I.

Rapic acid. By JULIUS ZELLNER (*Monatsh.*, 1896, **17**, 309—313).—Rapic acid, prepared by Reimer and Will's prescription (*Abstr.*, 1887, 1030), was treated with phosphorus triiodide, and the iodo-acid thus produced was hydrogenised by zinc and hydrochloric acid,

whereby stearic acid was obtained. This formation of stearic acid renders it unlikely that rapic acid has the formula $C_{18}H_{31}O_3$, which was assigned to it by Reimer and Will; for since it cannot be acetylated, and is not, therefore, a hydroxy-acid, it is not conceivable how one of the oxygen atoms can be eliminated by iodine. New analyses of zinc rapate confirm the author's view that the formula for this acid is $C_{18}H_{31}O_2$; the acid is not identical with oleic acid, since it does not give the elaidin reaction.

A. G. B.

Tautomerism of Ethylic Acetoacetate. By ISIDOR TRAUBE (*Ber.*, 1896, 29, 1715—1723).—The tautomeric forms of ethylic formylphenylacetate (Wislicenus, this vol., i, 552) behave in a remarkable manner to solvents. When the α - or hydroxyl-form is dissolved in alcohol, the density of the solution gradually increases for some time after the solution has been prepared. This appears to be due to the gradual passage of a portion of the compound into the β - or keto-modification. That such a change actually takes place is shown by the fact that the reaction given by the α -form with ferric chloride is much more intense in chloroform solution than in alcoholic solution. The β -form gives no coloration with ferric chloride. The author has found that ethylic acetoacetate also behaves in a similar manner with certain solvents. In this case, the reaction with ferric chloride, which is characteristic of the hydroxyl form, is most strongly marked in methylic alcohol, and becomes gradually less strong in the following solvents: ethylic alcohol, amylic alcohol, water, pyridine, and glycerol, dark red; acetone, light red; methylic acetate, light pink; ethylic acetate, ethylic ether, and paraldehyde, faint pink; methylal, benzene, chloroform, carbon bisulphide, and carbon tetrachloride, colourless. According to this, therefore, the solution in alcohol contains almost entirely the hydroxyl form, whilst that in chloroform contains the keto-form. It is also to be observed that the coloration in those solvents which favour the production of the hydroxyl form gradually increases, so that equilibrium between the two forms present is not reached at once.

Similar conclusions may be drawn from the density of the solutions. The hydroxyl form has the smaller molecular volume, and it is found that the solutions in methylic and ethylic alcohols gradually increase in density for some time after their preparation, whilst, on the other hand, those in benzene and ethylic acetate decrease. The results point to the fact that the aqueous solution contains more of the hydroxyl form than of the keto-form.

When a few drops of ferric chloride are added to ethylic acetoacetate, the solution becomes much more intensely coloured when it is heated, whilst, if it be cooled in solid carbonic acid and ether, the colour entirely disappears. This, therefore, shows that the keto-form is most stable at low temperatures, and is converted into the hydroxyl form by rise of temperature.

A. H.

Formation of Additive Products from the Sodium Compounds of Ethylic Formylacetate and Acetoacetate, and Nitroethane. By ARTHUR MICHAEL (*Ber.*, 1896, 29, 1794—1799).

—The author holds the view that in an action such as that of ethylic sodioformylacetate on phenylic isocyanate the sodium first unites with the carbonyl oxygen, and that subsequently the two free carbon bonds in the residues $\text{CHO}\cdot\dot{\text{C}}\text{H}\cdot\text{COOEt}$ and $\text{NPh}\cdot\dot{\text{C}}\cdot\text{ONa}$ unite. Similarly, the formation of nitromethaneazobenzene is not a case of substitution, but of addition of sodium to the most negative of the unsaturated nitrogen atoms of the diazo-salt, whereby a carbon and nitrogen bond are set free and reciprocally saturate one another; the sodium is subsequently eliminated as sodium chloride. A similar example is that of the reaction between sodium phenoxide and amylic nitrite (Walker, Abstr., 1884, 1003). The author extends this view to all cases of substitution in which an oxygenated radicle replaces a hydrogen atom combined with carbon. Numerous instances are cited in support of these views.

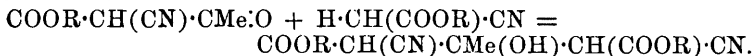
A. R. L.

Derivatives of Alkylcy Cyanacetates. By J. GUINCHANT (*Compt. rend.*, 1896, **122**, 1209—1212).—When alkylcy sodiocyanacetates act on an equivalent quantity of an acid chloride in presence of dry ether, a new series of compounds is formed. Their composition is equivalent to the sum of a molecule of acetocyanacetate and a molecule of cyanacetate, and the author provisionally terms them *acetylbicyanacetates*; they have a feeble acidic function, but do not decompose alkali carbonates.

Methylic acetylbicyanacetate, $\text{C}_{10}\text{H}_{12}\text{O}_5\text{N}_2$, melts at 101° , and its aqueous or alcoholic solution gives, with a trace of alkali, a beautiful, golden-yellow coloration, which fades after a time in the cold, and immediately on heating. With potassium hydroxide, a salt of a new acid is obtained, which melts at 240° .

Ethylic acetylbicyanacetate melts at 83° and crystallises from alcohol in large, monoclinic tables with six faces; pm , $96^\circ 30'$; mm , $122^\circ 45'$; pa , $49^\circ 20'$.

It is possible that, in the formation of these compounds, an aldol reaction takes place between the ketonic oxygen of the acetocyanacetate and the hydrogen attached to the same carbon as the carbonyl group of the cyanacetate;



Claisen has explained in the same way the formation of an analogous compound in the interaction between acetone, ethylic oxalate, and sodium. The same explanation would follow if it were assumed that ethylic acetocyanacetate is capable of existing in an enolic form, $\text{OH}\cdot\text{CMe}\cdot\text{C}(\text{CN})\cdot\text{COOR}$.

C. H. B.

Action of Isobutaldehyde on Malonic and Cyanacetic acids. By LUDWIG BRAUN (*Monatsh.*, 1896, **17**, 207—224).—The method of synthesising unsaturated acids by the condensation of malonic acid with acetaldehyde and propaldehyde has not been applied to the production of higher homologues. The author has therefore heated malonic acid with isobutaldehyde and glacial acetic acid containing 10 per cent. of the anhydride at 100° in a reflux apparatus, obtaining a mixture of

$\alpha\beta$ - and $\beta\gamma$ -isohexenoic acids, along with β -hydroxyisocaproic acid; the last-named substance is separated by submitting the product to distillation in a current of steam, which carries over the unsaturated acids.

β -Hydroxyisocaproic acid, $\text{CHMe}_2\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{COOH}$, is a colourless syrup, which dissolves readily in common solvents; the silver salt crystallises from hot water. On heating the acid under ordinary pressure, an oil distils at $203\text{--}220^\circ$, consisting principally of $\alpha\beta$ - and $\beta\gamma$ -isohexenoic acids, along with isocaprolactone.

$\alpha\beta$ -Isohexenoic acid, $\text{CHMe}_2\cdot\text{CH}:\text{CH}\cdot\text{COOH}$, is isolated by treating the mixture of unsaturated acids with dilute sulphuric acid, which converts the $\beta\gamma$ -modification into isocaprolactone (compare Fittig, Abstr., 1895, i, 204); it is a colourless liquid, which boils at $211\text{--}212^\circ$, and solidifies in solid carbonic anhydride. The calcium salt separates from water in white, silky crystals, and the silver salt crystallises in needles. Bromine converts the acid into $\alpha\beta$ -dibromisocaproic acid, which separates from carbon bisulphide in colourless crystals and melts at 127° . Oxidation with potassium permanganate in alkaline solution gives rise to $\alpha\beta$ -dihydroxyisocaproic acid, which crystallises from a mixture of ether and light petroleum in rosettes of colourless needles, and melts at 108° ; the calcium salt is anhydrous. β -Bromisocaproic acid is produced when $\alpha\beta$ -isohexenoic acid is treated with hydrogen bromide; it is liquid, and, when gently heated with aqueous sodium carbonate, yields isopropylethylene.

Isobutylidenecyanacetic acid, $\text{C}_7\text{H}_9\text{NO}_2$, is obtained by heating cyanacetic acid with isobutaldehyde (1 mol.) for eight hours in sealed tubes at 100° (compare Fiquet, Abstr., 1894, i, 32); it crystallises from light petroleum in long needles, and melts at $87\text{--}88^\circ$. The acid does not combine with bromine, and hot aqueous potash resolves it into isobutaldehyde, ammonia, and malonic acid. The calcium and silver salts crystallise in white needles, and the nitrile boils at 65° under a pressure of 20 mm.; bromine converts the nitrile into the dibromide, $\text{C}_6\text{H}_9\text{NBr}_2$, which melts at 30° , whilst hydrolysis with aqueous potash gives rise to ammonia, isocaprolactone, and a mixture of $\alpha\beta$ - and $\beta\gamma$ -isohexenoic acids. M. O. F.

Angelica Oil. By GIACOMO L. CIAMICIAN and PAUL SILBER (*Ber.*, 1896, 29, 1811—1816).—The authors have submitted to examination a heavy, brown, oily liquid representing the last runnings obtained by the distillation of angelica roots; this, after being left for some time, deposited a very small quantity of crystals which melted at $74\text{--}77^\circ$. The separated oil boiled between 125° and 230° under a pressure of 20 mm.; from the viscous residue, light petroleum extracted crystals melting at $68\text{--}70^\circ$. Both the latter and the crystalline compound deposited from the original oil appear to be anhydrides of a hydroxy-acid. The oil, which had been once fractionated under diminished pressure, was treated with alcoholic potash; the residual oil consisted for the most part of terpenes boiling at $240\text{--}270^\circ$. From the alkaline solution, on the addition of sulphuric acid, hydroxypentadecyclic acid, $\text{C}_{15}\text{H}_{30}\text{O}_3$, separated, which, after crystallisation from ether, melted at 84° ; the barium salt is a white powder, and the acetyl derivative

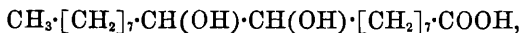
melts at 59°. *Bromopentadecyclic acid*, $C_{15}H_{29}BrO_2$, is obtained by heating the hydroxy-acid with concentrated hydrobromic acid; it melts at 65°. *Iodopentadecyclic acid* melts at 78—79°. Methyl-ethyl-acetic acid was isolated from the alkaline solution above mentioned after acidification.

A. R. L.

Preparation of Glyceric acid. By PAUL CAZENEUVE (*Compt. rend.*, 1896, **122**, 1206—1207).—When silver chloride is heated with excess of sodium hydroxide and glycerol, the latter is converted into glyceric acid without any formation of aldehydes; 144 parts of silver chloride, 46 parts of glycerol, and 80 parts of sodium hydroxide in 500 parts of water are convenient proportions. The silver chloride is first converted into the oxide and afterwards reduced to metallic silver. The glyceric acid is separated from the excess of glycerol by repeated treatments with dry acetone, in which glycerol is insoluble.

C. H. B.

Decomposition of Dihydroxystearic acid into its Optically Active Constituents. By PAUL FREUNDLER (*Bull. Soc. Chim.*, 1895, [3], **13**, 1052—1055).—Two *dihydroxystearic acids*,



are known, the one obtained from oleic and the other from elaidic acid (Gröger, *Abstr.*, 1885, 883, and Saytzeff, *Abstr.*, 1886, 140). These should be racemic modifications, and should be capable of being separated into four optically active dihydroxystearic acids. The author has succeeded in decomposing the acid (m. p. 131°) obtained from oleic acid into its optically active constituents by means of its strychnine salt. The acid is first converted into its potassium salt, which forms crystalline granules insoluble in water, but soluble in warm alcohol, and a boiling solution of the potassium salt is then mixed with an excess of strychnine sulphate, and warmed for about half an hour; the sulphate of potassium is filtered off, and the filtrate yields first of all crystals of the strychnine salt of the lævo-acid. After concentration, long needles of strychnine sulphate separate out and finally crystalline granules of the strychnine salt of the dextro-acid. The separation is almost complete, and the salts need not be further purified. The acids themselves are readily obtained by decomposing these salts with concentrated hydrochloric acid; both are very sparingly soluble in most solvents at the ordinary temperature. The *ethylic salt* of the lævo-acid crystallises in colourless needles, melts at 98—99°, and has a specific rotatory power $[\alpha]_D = -2.1^\circ$. The corresponding *strychnine salt* crystallises with $5H_2O$, and melts at 128—130°. The *ethylic salt* of the dextro-acid resembles that of the lævo-acid, but has a specific rotatory power $[\alpha]_D = +1.6^\circ$. These numbers are only approximate, as the solutions used were extremely dilute owing to the slight solubility of the ethylic salt.

J. J. S.

Velocity of Lactone Formation amongst Acids of the Sugar Group. By EDVARD I. HJELT (*Ber.*, 1896, **29**, 1861—1863).—Attention has already been drawn to a variation in velocity of lactone

formation amongst certain sugar acids, and the author has determined the velocity constants for *l*-mannonic, *l*-gulonic, α -glucoheptonic, *l*-arabonic, saccharic, and mucic acids. In the case of gluconic acid, the production of a lactone is so slow, and the regeneration of the hydroxy-acid so rapid, that accurate results could not be obtained by titration.

M. O. F.

Acid Peroxides and their action on reducing Substances.

By LUDWIG VANINO and EDMUND THIELE (*Ber.*, 1896, **29**, 1724—1729).—A number of acid peroxides have been prepared by the method of Pechmann and Vanino (*Abstr.*, 1894, i, 416).—*Succinic peroxide*, $C_4H_4O_4$, is a white, crystalline compound, which is insoluble in all the usual solvents, and explodes violently when heated to 120° in a narrow tube. It also explodes when rubbed or pressed in the dry state. It has strong oxidising properties, and explodes when treated with aniline or strong sulphuric acid. Phenylhydrazine also reacts violently with the peroxide, but in dilute solution converts it into succinimide. Benzoic peroxide, on the other hand, when treated in the same way yields *benzoylphenylhydrazine*, which crystallises in asymmetric tablets melting at 168 — 170° .

Benzoic peroxide does not liberate sulphur from sodium thio-sulphate or decolorise potassium permanganate solution, but otherwise resembles succinic peroxide in its oxidising properties.

Fumaric peroxide, $C_4H_2O_4$, is a white, insoluble powder, which detonates faintly at 80° , but otherwise closely resembles the succinic compound.

Acetic peroxide could not be obtained in the solid state. *Phenyl-acetic peroxide* is soluble in ether, and melts at 41° . It does not appear to be explosive, but decomposes so readily with formation of phenylacetic acid that it could not be obtained pure.

Orthotoluic peroxide crystallises from dilute alcohol in indistinct prisms, melting at 60° . It shows all the characteristic properties of the peroxides.

Camphoric peroxide appears to be extremely unstable. A. H.

Action of Ethylic Iodide and Zinc on Ethereal Salts of $\Delta^{\alpha\beta}$ -Unsaturated Aliphatic acids. By ARTHUR MICHAEL (*Ber.*, 1896, **29**, 1791—1792).—Ethylic fumarate, ethylic iodide, and zinc, when digested together for a long time, yield *ethylic ethylsuccinate*, boiling at 230 — 231° . In the same way, ethylic ethylfumarate, boiling at 122 — 123° at 15 mm., is obtained from ethylic acetylenedicarboxylate and ethylic iodide; whilst if the portion of the product from ethylic citraconate and ethylic iodide which boils between 235° and 237° is hydrolysed, symmetrical methylethylsuccinic acid (m. p. 174 — 175°) is obtained. The yield obtained by this method is 20—25 per cent. of the theoretical, whilst the main products of the reaction are compounds of an acid and neutral nature, the investigation of which is not yet complete.

A. R. L.

Synthesis of Camphoronic acid and its Derivatives. By GUSTAV KOMPPA [and A. BERGROTH] (*Ber.*, 1896, **29**, 1619—1625).—

The results obtained in this investigation on the synthesis of hydroxytrimethylsuccinic acid and its derivatives are in the main the same as those obtained by Anwers and von Campenhausen (this vol., i, 525). A. L.

Hydrolysis of the Alkyl Substitution Derivatives of Ethylic Malonate. By EDVARD I. HJELT (*Ber.*, 1896, 29, 1864—1867; compare this vol., i, 205).—The rates of hydrolysis of ethylic isobutylmalonate and isopropylmalonate have been revised, and the values for ethylic methylmalonate, phenylmalonate, ethylallylmalonate, and propylallylmalonate, determined. The rates of hydrolysis are lower for dialkyl derivatives than for monalkyl, and this property is not correlative with the affinity constant for the acid, but is most probably influenced by steric conditions.

The author discusses his results in the light of Victor Meyer's theory of ethereal salt formation. M. O. F.

Alkylated Valerolactones. By EDVARD I. HJELT (*Ber.*, 1896, 29, 1855—1859).—In order to study the influence of alkyl groups on the velocity of lactone formation, the author has prepared substituted allylactic acids, and converted them into the respective lactones; the syntheses were effected by means of ethylic allylmalonate.

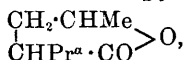
Ethylallylmalonic acid is obtained from ethylic allylmalonate, ethylic bromide, and sodium ethoxide, and separates from benzene in large, transparent crystals melting at 107—108°; the *ethylic salt* boils at 233°. Elimination of carbonic anhydride, which occurs at 150°, gives rise to *ethylallylactic acid*, which boils at 208°.

Propylallylmalonic acid crystallises from benzene in microscopic needles, and melts at 115°; the *ethylic salt* boils at 240—241°. Heat converts it into *propylallylactic acid*, which boils at 221°.

Isopropylallylmalonic acid closely resembles the normal derivative, and melts at 112.5°; the *ethylic salt* boils at 232—238°. *Isopropylacetic acid* boils at 217°, and has a rancid odour. The electrical conductivity constants of propyl- and iso-propylallylmalonic acids, $K = 0.93$ and $K = 1.46$ respectively, approximate to those of other substituted malonic acids (compare Walden, *Abstr.*, 1892, 266).

The lactones were obtained by Fittig's method, treating the unsaturated, monobasic acids with hot, dilute sulphuric acid during 15 minutes, diluting with water, heating again, and finally extracting with ether; the liquid was then agitated with soda, evaporated, and the residue dried by means of potassium carbonate.

Ethylvalerolactone, $\begin{array}{c} \text{CH}_2\cdot\text{CHMe} \\ | \\ \text{CHEt}\cdot\text{CO} \end{array} > \text{O}$, boils at 216°, and has the characteristic odour of volatile lactones. *Propylvalerolactone*,



boils at 233°, and *isopropylvalerolactone* at 224°.

On determining the velocity coefficients of these lactones, the hydroxy-acids were found to arrange themselves in the following

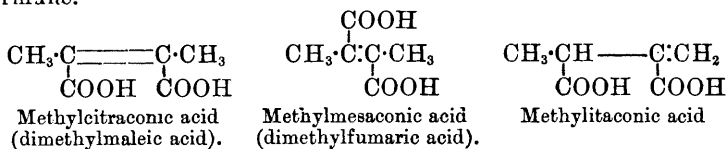
order— γ -Hydroxyvaleric acid, $Ac = 0.0027$; isopropyl- γ -hydroxyvaleric acid, $Ac = 0.0085$; propyl- γ -hydroxyvaleric acid, $Ac = 0.0100$; ethyl- γ -hydroxyvaleric acid, $Ac = 0.0104$. M. O. F.

Intramolecular Change in Unsaturated Acids. The Isomerides of Pyrocinchonic [Dimethylmaleïc] acid. By RUDOLPH FITTIG (*Ber.*, 1896, **29**, 1842—1843).—Dimethylmaleïc (pyrocinchonic) acid, existing only in the form of the anhydride, has not been hitherto converted into the fumaric modification, and Delisle states that soda has no action on it (*Abstr.*, 1892, 297). This, however, is not the case, and two new acids have been obtained from the anhydride of dimethylmaleïc acid under the influence of 20 per cent. aqueous soda.

Dimethylfumaric (methylmesaconic) acid, $C_6H_8O_4$, crystallises in feathery aggregates of long needles, and dissolves sparingly in water; it melts at 240° , and sublimes below this temperature without undergoing decomposition. The *barium* salt crystallises in colourless needles.

Methylitaconic acid, $C_6H_8O_4$, is more readily soluble in water, and crystallises in monosymmetric prisms; it melts at 150 — 151° , and in part decomposes, undergoing conversion into dimethylmaleïc anhydride and water when distilled. The *barium* salt, which contains $1H_2O$, dissolves with great difficulty in hot water, but is less sparingly soluble in cold water.

The configuration of the three acids is represented by the following formulæ.



M. O. F.

Constitution of Oxalacetic acid. By ARTHUR MICHAEL and JOHN E. BUCHER (*Ber.*, 1896, **29**, 1792—1793).—Both ethylic oxalacetate and the ethylic derivative of asymmetrical diethoxysuccinic acid are quantitatively converted into oxalacetic acid by cold concentrated hydrochloric acid; the latter, when warmed with acetic chloride or acetic anhydride, yields acetoxymaleïc anhydride (this vol., i, 85). Nef's ethylic ethoxymaleïc acid (*Abstr.*, 1893, i, 628), when hydrolysed with hydrochloric acid, gives oxalacetic acid, but if hydrolysed with cold, dilute alkali, it gives ethoxymaleïc acid (m. p. 132 — 134°), which yields the liquid anhydride of ethoxymaleïc acid on treatment with acetic anhydride. Ethoxymaleïc acid likewise yields oxalacetic acid on treatment with hydrochloric acid. Ethylic dibromosuccinate gives ethylic ethoxymaleïc acid, together with a little ethylic diethoxysuccinate when treated with sodium ethoxide (2 mols.); if more ethoxide is employed, the relative amounts of the two products are reversed. Ethylic acetylenedicarboxylate, when treated with cold sodium hydroxide, gives a mixture of the ethylic derivatives of asymmetrical diethoxysuccinic acid, ethoxymaleïc

acid, and ethoxymaleic acid, whereas, at a higher temperature, only the two latter are formed.

The formation of oxalacetic acid by warming asymmetrical diethoxysuccinic acid, by the action of hydrochloric acid on ethoxymaleic acid, and that of water on acetoxymaleic anhydride shows that it contains no carbonyl groups. If that were so, oxalacetic acid would be acetoxymaleic anhydride, whereas, according to its formation from ethylic ethoxymaleate, it must be hydroxymaleic acid; it should also be remarked that the conversion of a fumaroid modification into a maleinoid, by means of hydrochloric acid, has not yet been observed, besides which the stability of oxalacetic acid towards hydrochloric acid is incompatible with the assumption that it is the maleinoid modification. The apparent anomaly of these reactions vanishes if it be assumed that the primarily formed hydroxy-acids are labile and change into $\text{COOH} \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{COOH}$. The ketone constitution must also be assigned to ethylic oxalacetate.

A. R. L.

Two Stereoisomeric Methylcarbocaprolactonic acids. By EDVARD I. HJELT (*Ber.*, 1896, **29**, 1860—1861; compare *Abstr.*, 1892, 697).—*Paramethylcarbocaprolactonic acid*, $\text{C}_8\text{H}_{12}\text{O}_4$, is obtained from both para- and μ -methylallylsuccinic acid (*loc. cit.*) by means of Fittig's method for producing lactones; it crystallises from water in well-defined prisms, and melts at 140—141°. The barium salt is crystalline.

μ -*Methylcarbocaprolactonic acid* separates on allowing the oily mother liquor of the foregoing acid to deposit crystals; it forms needles melting indefinitely at 60—68°, and dissolves very readily in water. The barium salt is crystalline.

M. O. F.

Hydrolysis of Ethereal Salts of certain Tribasic acids. By EDVARD I. HJELT (*Ber.*, 1896, **29**, 1867—1869; compare this vol., i, 205, and 598).—The rates of hydrolysis of ethylic salts of ethanetricarboxylic, propanetricarboxylic, phenylethanetricarboxylic, ethylethanetricarboxylic, and allylpropanetricarboxylic acids have been determined, and found to diminish in the order indicated. The values for triethylic citrate, aconitate, and camphoronate diminish in the order named.

The author's experiments with dibasic and tribasic acids render it

probable that the grouping $\begin{array}{c} \text{C} \\ | \\ \text{C} \cdot \text{C} \cdot \text{C} \\ | \\ \text{COOEt} \end{array}$ is not favourable to hydrolysis;

if this indication is trustworthy, the rate of hydrolysis of triethylic camphoronate favours representation of the acid by Bredt's formula rather than Tiemann's.

M. O. F.

Formation of Carbon Chains. XII. Quantitative Study of the Synthesis of Ethereal Salts of Penta-, Hexa-, and Heptabasic Fatty acids. By CARL A. BISCHOFF (*Ber.*, 1896, **29**, 1741—1750).—The interaction of methylic sodethanetricarboxylate and methylic bromomalonate proceeds in the normal manner, 51 per cent.

of the product consisting of *methylic propargylpentacarboxylate* (pentandioic-2 : 2 : 3-trimethyloate; propane-1 : 2 : 2 : 3 : 3-pentacarboxylate), which crystallises in four-sided tablets melting at 87—88°. Hydrolysis with hydrochloric acid yields tricarballic acid. When the corresponding ethylic salt is treated with ethylic chloromalonate, only 7 per cent. of the normal product is formed, along with a little ethylic ethanetetracarboxylate. When the product is washed with water, a portion of the substance becomes hydrolysed, and goes into solution, but the nature of the products formed has not yet been ascertained. The normal product is also formed, to the extent of about 40 per cent., from the ethylic salt and ethylic bromomalonate.

In the case of the ethereal salts of ethanetetracarboxylic acid, no normal product was obtained by the interaction of the ethylic salts and the chloromalonate, about 70 per cent. from the methylic salts and the bromomalonate, and only a very small quantity from the ethylic salts and the bromomalonate, the chief products being ethylic ethanetetradicarboxylate and ethylenetetracarboxylate. This result is quite in accordance with the author's dynamical theory, according to which the nature of the alkyl group should have a special influence on the formation of this ethereal salt. Hydrolysis with hydrochloric acid yields tricarballic acid.

The formation of the normal product (heptabasic) from ethylic sodiopropane-1 : 2 : 2 : 3 : 3-pentacarboxylate and ethylic bromomalonate could not be definitely proved, since considerable decomposition took place on distillation. No evidence of the formation of butanetetracarboxylic acid, on hydrolysis, could be obtained.

A. H.

Constitution of Acid Amides. By ARTHUR LACHMANN (*Amer. Chem. J.*, 1896, **18**, 600—608).—A study of the work which has been done on this question leads the author to the conclusion that the amides fall into two classes—(1) those possessing the ordinary amide formula; such are probably oxamethane, the various carbamides and benzenesulphonamide; and (2) those which have the imido-hydroxy-structure; such are probably acetamide and benzamide. In order to obtain further evidence, the behaviour of amides towards sundry reagents was examined, but without results worthy of discussion, except in the case of phosphorus trichloride. With this reagent, acetamide gives a red, sticky mass containing chlorine, phosphorous acid, ammonia, and acetamide; hydrogen chloride is evolved, but neither acetonitrile nor acetic chloride is formed. Benzamide gives 75 per cent. of bezonitrile. Urethane is destroyed. Oxamethane remains unchanged. This production of benzonitrile from benzamide cannot be a case of mere dehydration, since oxamethane is as sensitive to dehydrating agents as is benzamide, and yet it is not affected by the trichloride. In the author's opinion the benzamide forms an imido-chloride as an intermediate product, and must, therefore, contain a hydroxyl group.

A. G. B.

Action of Nitric acid on Methylamides and Dimethylamides. By ANTOINE P. N. FRANCHIMONT (*Rec. Trav. Chim.*, 1896, **15**, 61—65; VOL. LXX. i.

2 x

compare Abstr., 1888, 447).—Absolute nitric acid may behave with methylamides and dimethylamides of different acids in one of four different ways.

I. Neither the methylamide nor the dimethylamide is acted on. Examples: Those of nitrobenzoic acid, trichloroacetic acid; in the case of the latter, however, the monomethylamide is very slowly acted on, but the dimethylamide not at all. A special case is met with in certain derivatives of oxalic acid; dimethyloxamide readily yields a nitro-derivative, whereas tetramethyloxamide is not acted on.

II. The methylamide yields the corresponding acid, nitric peroxide, and methylic nitrate, whilst the dimethylamide yields the acid and dimethylnitramine. Examples: Trimethylacetic, heptilic, succinic, dimethylmalonic, amidiformic acids, &c.

III. The methylamide yields a stable nitro-derivative, whereas the dimethylamide yields the acid and dimethylnitramine. Examples: Phenylsulphonic, ethylsulphonic, and sulphuric acids.

IV. The methylamide gives a stable nitro-derivative, whilst the dimethylamide undergoes oxidation; one of the methyl groups is removed, and becomes replaced by a nitro-group in such a manner that the dimethylamide yields the same nitro-derivative as the methylamide. Examples: Picric acid, dinitrocresols (ortho- and para-), trinitrometacresol, the methylic and ethylic salts of mono- and di-methylamidiformic acid, which yield in this way nitro-urethanes.

These differences in behaviour must be attributed to the influence of the different negative radicles. J. J. S.

Action of Nitric acid on Oxalpiperidide. By ANTOINE P. N. FRANCHIMONT and H. VAN ERP (*Rec. Trav. Chim.*, 1896, **15**, 66—68).—Oxalpiperidide, for the preparation of which compare Schotten (Abstr., 1882, 983), and Kamensky (*Annalen*, 1882, **214**, 278), readily dissolves in pure nitric acid; very little heat is developed, and the solution is only slightly coloured. No disengagement of gas occurs, and the liquid, when placed in a vacuum for a few days, yields the unaltered piperidide in almost theoretical quantity. Oxalpiperidide thus behaves towards nitric acid like tetramethyloxamide. (Compare previous abstract.) J. J. S.

Action of Nitric acid on certain Piperidides. By ANTOINE P. N. FRANCHIMONT and H. J. TAVERNE (*Rec. Trav. Chim.*, 1896, **15**, 69—75).—The piperidides of oxalic and of alkylcarbonic acids react with nitric acid similarly to the dimethylamides of the corresponding acids. Thus oxalpiperidide is not acted on (see preceding abstract), whereas piperylurethane is oxidised, and at the same time nitrated (*Rec. Trav. Chim.*, 1894, **13**, 334). The authors have prepared three more piperidides, and studied their action towards nitric acid.

Trichloroacetopiperidide was obtained by the action of an ethereal solution of trichloroacetic chloride on an ethereal solution of piperidine; it forms large, colourless crystals, melts at 45°, and is insoluble in water, and not decomposed when boiled with the same. It dissolves in ether, alcohol, chloroform, benzene, &c., readily forms super-

saturated solutions in ether or in light petroleum, and is not acted on by cold nitric acid.

Benzenesulphonopiperidide (Hinsberg, Abstr., 1892, 65), and Schotten (Abstr., 1892, 354), when treated with cold nitric acid, is decomposed in much the same way as benzenesulphonodimethylamide (*Rec. Trav. Chim.*, 1883, 3, 7), and nitropiperidine is one of the products formed.

Picrylpiperidide (Turpin, Trans., 1891, 59, 716, and Schotten, *loc. cit.*), when added to ice-cold nitric acid, is readily acted on, and yields *picrylnitrodehydropiperidide*; this crystallises from alcohol in red needles, melts at 195°, and is hydrolysed when boiled with a 10 per cent. potash solution. J. J. S.

“**Carbothioacetoinin.**” By JOHANN HEILPERN (*Monatsh.*, 1896, 17, 229—244).—This name was applied by Städeler (*Annalen*, 1859, 111, 311, 316) to the compound which Hlasiwetz prepared by the interaction of acetone, carbon bisulphide, and ammonia (*ibid.*, 1850, 76, 294). The author has prepared the compound, and finds that its molecular formula is $C_7H_{14}N_2S$, and that when oxidised by potassium permanganate, it yields acetonylearbamide, thus justifying the conclusion that it is *pinacolylthiocarbamide*, $\begin{matrix} CMe_2 \cdot NH \\ | \\ CMe_2 \cdot NH \end{matrix} > CS$. The compound

crystallises in microscopic, colourless, four-sided, pointed prisms, melts at 240—243° (uncorr.), and dissolves freely in hot alcohol, ether, ethylic acetate, acetone, chloroform, hydrochloric acid, and glacial acetic acid. It is intensely bitter, and chemically indifferent. The *platinochloride* of an *ethyl* derivative $(C_7H_{13}EtN_2S)_2 \cdot H_2PtCl_6$, was found to crystallise in small, orange-red tables, and to melt at 161—163° (uncorr.), but the ethyl derivative itself could not be purified, nor could any other well characterised substitution product be isolated.

Acetonylearbamide *aurochloride* has the anomalous composition $(C_5H_8N_2O_2)_2 \cdot HAuCl_4 + 2H_2O$, similar to that found by Heintz for the gold salt of carbamide (*ibid.*, 1880, 202, 264); it melts at 161—162° (uncorr.). A. G. B.

Condensation of Ketopentamethylene with Aldehydes. By DANIEL VORLÄNDER and KARL HOBBOHM (*Ber.*, 1896, 29, 1836—1841).—The ketone, C_6H_8O , isolated from the higher boiling fraction of wood spirit, has been shown by Hentzschel to be adipin ketone (Abstr., 1893, i, 556), and is therefore the cyclic analogue of diethyl ketone. The authors have compared the behaviour of these two substances towards aldehydes, having already shown (this vol., i, 546) that diethyl ketone combines with benzaldehyde (2 mols.), forming the anhydride of a ketoglycol. This substance, which is also produced by the action of benzaldehyde on benzylidenediethyl ketone, has the constitution, $\begin{matrix} CHMe \cdot CO \cdot CHMe \\ | \quad \quad | \\ CHPh - O - CHPh \end{matrix}$, and thus the behaviour of diethyl ketone towards benzaldehyde is shown to be quite different from that of acetone; in this respect, however, ketopentamethylene

is found to resemble the latter ketone, yielding a dibenzylidene compound, instead of a derivative of pyrone.

Dibenzylideneketopentamethylene, $\text{CO} < \begin{smallmatrix} \text{C}(\text{CHPh})\cdot\text{CH}_2 \\ \text{C}(\text{CHPh})\cdot\text{CH}_2 \end{smallmatrix}$, obtained by dissolving adipin ketone and benzaldehyde (2 mols.) in 50 per cent. alcohol, crystallises in yellow needles, melting at 189° ; reduction with zinc dust and glacial acetic acid gives rise to a white substance, which probably consists of dibenzylketopentamethylene. The *tetrabromide*, $\text{C}_{19}\text{H}_{16}\text{Br}_4\text{O}$, crystallises from glacial acetic acid in needles, and melts, evolving hydrogen bromide, at 175° ; when the alcoholic solution is boiled with powdered antimony, dibenzylideneketopentamethylene is regenerated. *Benzylideneketopentamethylene*, $\text{C}_{12}\text{H}_{12}\text{O}$, forms colourless crystals, and melts at 68° .

Dianisylideneketopentamethylene, $\text{C}_{21}\text{H}_{20}\text{O}_3$, crystallises from absolute alcohol in lustrous, yellow plates, and melts at 212° . *Dicinnamylideneketopentamethylene* is yellow, and melts at $215\text{--}218^\circ$.

Difurfurylideneketopentamethylene, $\text{C}_{15}\text{H}_{12}\text{O}_3$, is the pyroxanthin of Scanlan, Apjohn, and Gregory, and melts at 163° ; the solution in concentrated sulphuric acid is intense violet-blue, the moderately concentrated acid yielding a carmine-red solution. Treatment with excess of bromine in carbon bisulphide solution gives rise to *dibromopyroxanthin tetrabromide*, $\text{C}_{15}\text{H}_{10}\text{Br}_6\text{O}_3$, which crystallises from chloroform in colourless needles; when heated at $90\text{--}100^\circ$, it blackens, but if the temperature is quickly raised to 150° , it becomes grey, melts, and effervesces vigorously. Hot phenol, or boiling alcohol with zinc dust or antimony, converts the tetrabromide into dibromopyroxanthin (Hill, 1876, ii, 456), which melts at 180° .

Difurfurylideneketohexamethylene crystallises from alcohol in yellow needles, and melts at 144° ; the solution in concentrated sulphuric acid is violet, and in moderately strong acid, carmine-red. *Dibenzylideneketohexamethylene* crystallises in yellow prisms, and melts at 118° .

The application of benzaldehyde in separating the constituents of wood oil and acetone oil is recommended by the authors, who have isolated from the latter a compound which crystallises in needles, and melts at 233° .
M. O. F.

Direct Substitution of Chlorine or Bromine for Nitro-groups by the Aid of Hydrochloric or Hybromic acid. By CORNELIS A. LOBRY DE BRUYN and FREDERIK H. VAN LEENT (*Rec. Trav. Chim.*, 1896, 15, 84—88).—The authors find that various nitro-compounds (1—2 grams) when heated with saturated aqueous hydrochloric acid (2—3 c.c.) at $200\text{--}300^\circ$ for several hours yield products which contain chlorine in place of the nitro-groups. These chloro-derivatives are best separated from the unaltered nitro-compounds by distillation with steam. Symmetrical trinitrobenzene yields the corresponding trichlorobenzene and a small quantity of tetrachlorobenzene. Orthodinitrobenzene, heated at $250\text{--}270^\circ$ for an hour and a half, yields orthodichlorobenzene. Metadinitrobenzene yields a mixture of meta-dichloro- and trichloro-benzene. Paradinitrobenzene and parachloronitrobenzene both yield paradichlorobenzene. δ -Tetranitronaphtha-

lene (1 : 2 : 1 : 4') yields the corresponding tetrachloronaphthalene, but γ -tetranitronaphthalene yields a pentachloronaphthalene. Symmetrical trinitrobenzoic acid yields symmetrical trichlorobenzene. The nitrophenols are not acted on at 220°, and at higher temperatures are completely decomposed.

Orthodinitrobenzene, when heated with hydrobromic acid at 250—260°, yields orthodibromobenzene. J. J. S.

Electrolytic Reduction of Nitrobenzene in presence of Hydrochloric acid. By WALTER LÖB (*Ber.*, 1896, 29, 1894—1899; compare this vol., i, 533).—When nitrobenzene suspended in hydrochloric acid is placed in a porous cylinder, which is surrounded by dilute sulphuric acid, and a current of 0.6—1 ampère and 5—5.5 volts passed through, an anode of platinum being placed in the sulphuric acid, the nitrobenzene is reduced, with formation of a mixture of ortho- and para-chloraniline. It seems probable that phenylchloramine, C_6H_5NHCl , is formed as an intermediate compound, but direct evidence of this has not yet been obtained. The reduction can also be carried out spontaneously by placing the nitrobenzene and hydrochloric acid in a porous cylinder surrounded by an acid solution of ferrous sulphate, and connecting a carbon rod placed in the cylinder with an amalgamated zinc plate placed in the ferrous sulphate solution. About 20 per cent. of the nitrobenzene appears to undergo some other change, the exact nature of which has not yet been ascertained.

When a solution of nitrobenzene in alcoholic hydrochloric acid is treated in a similar way, the chief product is benzidine, azobenzene and chloraniline being also formed. A. H.

Orthohalogen Derivatives of Nitrobenzene and of Orthamidophenylic Ethers. By F. ULLMANN (*Ber.*, 1896, 29, 1878—1881).—Orthochloronitrobenzene is best prepared by means of Sandmeyer's reaction, "bronze powder," washed with ether, being used instead of precipitated copper; a yield of 65 per cent. is obtained. Orthobromonitrobenzene, which melts at 41.5° and boils at 260° (pressure = 734 mm.), may be prepared in a similar way, nearly 70 per cent. of the theoretical yield being obtained. A quantitative yield of orthiodonitrobenzene, which boils at 288—289° (pressure = 729 mm.) and melts at 49.5°, is obtained in the same way. *Orthamidophenylic ether* may be readily obtained by the reduction of the corresponding nitro-compound with stannous chloride and hydrochloric acid. It boils at 307—308° (pressure = 728 mm.), and melts at 42.5—43°. The *hydrochloride* melts at 151.5°. A. H.

Preparation of Orthoisopropylphenol and of Jacobsen's Metapropylphenol. By PIERRE H. BAYRAC (*Bull. Soc. Chim.*, 1895, [3], 13, 981—984).—The author contradicts Claus and Schulte's statement (*Abstr.*, 1887, 264) that when cumene is treated with sulphuric acid for four days on the water bath, it yields more ortho- than para-sulphonic acid; he states that 100 grams of cumene treated according to Claus and Schulte's method never yields more

than 25 grams of the barium salt of the ortho-acid. *Orthoisopropylphenol* was prepared by fusing the potassium salt of the cumene-orthosulphonic acid with three times its weight of potash. The indophenol derivative could not be obtained in a crystalline form.

The author gives minute details for the preparation of Jacobsen's metapropylphenol (Abstr., 1878, 731), as considerable care has to be taken.

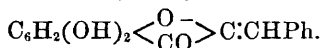
The indophenol of Jacobsen's compound has been prepared by the general method previously described (Abstr., 1895, i, 416); it melts at 73—74°. J. J. S.

Isopropylbenzoquinone. Constitution of Jacobsen's Metapropylphenol. By PIERRE H. BAYRAC (*Bull. Soc. Chim.*, 1895, [3], 13, 984—985).—*Isopropylbenzoquinone* crystallises in yellow prisms, melts at 28·4°, but when once fused does not readily solidify. It is very volatile, and is readily decomposed both by heat and light; it is sparingly soluble in cold water, but readily in alcohol, ether, and benzene. The quinone is readily reduced by sodium hydrogen sulphite solution saturated with sulphurous acid, and yields *isopropylquinol*, which crystallises in long, hard, transparent needles, and melts at 130—131°.

The indophenol derivative of Jacobsen's metapropylphenol has yielded the above quinone under the usual treatment (Abstr., 1895, i, 416), it therefore follows that Jacobsen's metapropylphenol is really metaisopropylphenol. J. J. S.

Paracymoquinone. By PIERRE H. BAYRAC (*Bull. Soc. Chim.*, 1895, [3], 13, 979—980).—This quinone, which is isomeric with thymoquinone, is best obtained by treating the indophenol derived from α -hydroxyparacymene according to the general method (Abstr., 1895, i, 416). It is a yellowish-red liquid heavier than water, and does not solidify at -15° , but when suddenly cooled by means of a jet of methylic chloride, it solidifies to bright golden needles, which melt at 18° . It is readily acted on by light, is rapidly changed when exposed to the air, and is decomposed on heating. It is only very sparingly soluble in water, but readily in alcohol and ether. It is readily reduced to the corresponding *quinol* by means of a solution of sodium hydrogen sulphite saturated with sulphurous acid; the quinol crystallises in brilliant plates, melts at 138° , and is readily oxidised back to the quinone. J. J. S.

Action of Benzaldehyde on Chloracetopyrogallol. By LUDWIG KESSELKAUL and STANISLAUS VON KOSTANECKI (*Ber.*, 1896, 29, 1886—1891).—The authors consider that the substance described as dihydroxyflavone (Friedländer and Rüdtt, *this vol.*, i, 439) which is formed by the action of benzaldehyde on chloracetopyrogallol, or anhydroglycogallol, is in reality *benzylideneanhydroglycogallol*,



The compound does not agree with the flavone derivatives in many

of its properties, thus it yields an orange-red and not a yellow solution in sulphuric acid, it dyes orange and not yellow on an alumina mordant, and it yields a yellow and not a colourless *diethyl ether*; the latter melts at 115° , and forms long, yellow needles. The compound is, moreover, formed by the direct action of benzaldehyde on anhydroglycogallol in presence of dilute potash.

Resacetophenone and its monethyl ether do not condense with benzaldehyde in presence of dilute aqueous soda, whereas the diethyl ether, under these circumstances, yields 2:4-diethoxybenzylideneacetophenone, $C_6H_3(OEt)_2CO \cdot CH:CHPh$, which forms long, pointed crystals, and melts at $92-93^{\circ}$.
A. H.

Flavone Derivatives. II. By PAUL FRIEDLÄNDER and HERMANN RÜDT (*Ber.*, 1896, 29, 1751—1756; compare this vol., i, 439).—

Anhydroglycopyrogallol, $C_6H_2(OH)_2 < \overset{O}{\underset{CO}{\parallel}} > CH_2$, like indoxyl, reacts with benzaldehyde to form the dihydroxyflavone already described. With isatin, it reacts to form an analogous derivative, $C_{16}H_9NO_5$, which crystallises in flat, reddish-brown needles, and dyes wool mordanted with chromium a brownish-violet. The triacetyl derivative crystallises in yellowish-red needles, and melts at 227° .

These compounds closely resemble chrysin in properties, and hence probably have the constitution assigned, and are not simple condensation products. This constitution is also rendered probable by the analogy of the derivatives of bromoresacetophenone and bromopeonol.

Diacetylbromoresacetophenone crystallises in colourless needles, melting at 38° , and, when treated with bromine in acetic acid solution, yields monobromodiacetylbromoresacetophenone, $C_6H_3(OAc)_2CO \cdot CH_2Br$. When this compound is boiled with aqueous soda, it yields a compound of the formula $C_6H_3(OH) < \overset{O}{\underset{CO}{\parallel}} > CH_2$, which crystallises in white, sparingly soluble needles, and melts and decomposes at 243° . This substance reacts with aldehydes in a similar manner to anhydroglycopyrogallol. Condensation products have been obtained with benzaldehyde, furfuraldehyde, and a number of other substances.

Bromoresacetophenone, $C_6H_3(OH)_2CO \cdot CH_2Br$, loses hydrogen bromide and passes into an anhydride, which yields the same condensation products with aldehydes as the original bromo-compound.

Bromopeonol, $OMe \cdot C_6H_3(OH) \cdot CO \cdot CH_2Br$ [$OMe : OH : CO \cdot CH_2Br = 4 : 2 : 1$], cannot be converted into an anhydride, but yields condensation products with aldehydes, which are quite analogous to those already described. This is a strong argument in favour of the flavone constitution of these derivatives, since the formation of a substance of the constitution $OMe \cdot C_6H_3 < \overset{O}{\underset{CO}{\parallel}} > C:CHPh$ would seem to require the intermediate formation of an anhydro-compound.

Monobromodiacetylpeonol, $OMe \cdot C_6H_3(OAc)CO \cdot CH_2Br$, melts at $86-87^{\circ}$. Its condensation products with aldehydes are yellowish. The piperonaldehyde derivative melts at 175° .
A. H.

New Apiole By GIACOMO L. CIAMICIAN and PAUL SILBER (*Ber.*, 1896, 29, 1799—1811).—The highest boiling fraction of a sample of dill oil, representing about 30 per cent. of the total oil, was submitted to fractional distillation under a pressure of 11 mm. About two-thirds passed over at 162°, and consisted of a new *apiole*; this differs from ordinary apiole from parsley in the position of the methylene relative to the methoxy-groups. It is an oily liquid, which could not be solidified by cooling, and boils at 285° under the ordinary pressure, decomposing slightly; it is almost insoluble in water, but dissolves in other ordinary solvents. Aqueous alkalis do not attack it, and it exhibits the same behaviour towards concentrated sulphuric acid as ordinary apiole. The *monobromodibromide*, $C_{12}H_{13}Br_3O_4$, crystallises in white needles, and melts at 110°.

When the new apiole is heated at 150—170° with sodium ethoxide for 6—10 hours an isomeric *isoapiole* is formed by reason of the transformation of the allyl group into the propenyl group; a phenolic compound is formed as a bye-product. The isoapiole crystallises from light petroleum in colourless, monoclinic prisms,

$$a : b : c = 0.86863 : 1 : 0.46102; \beta = 79^\circ 30',$$

melts at 44°, and boils at 296° with slight decomposition; it gives a red coloration with concentrated sulphuric acid. The *monobromobromide* melts at 115°. The bye-product, which is probably identical with the compound obtained in a similar manner from ordinary isoapiole (Bartolotti, *Abstr.*, 1892, 1315), boils at 189—191° under a pressure of 16 mm. The composition which Bartolotti has assigned to his substance is, in the author's opinion, inaccurate; thus, when apionol is methylated and subsequently oxidised with dilute permanganate, it yields *trimethylapionolic acid*, $OH \cdot C_6H(OMe)_3 \cdot COOH$, which melts at 139—140°. It appears to have the same constitution as the phenol obtained from isosafrole (*Abstr.*, 1892, 972).

On oxidation with permanganate, isoapiole from dill oil behaves similarly to isoapiole from parsley, and yields apiolic acid, apiolaldehyde, and apioleketonic acid. Whereas apioleketonic acid yields, on fusion with potash, apion (m. p. 79°), the corresponding acid from dill oil yields a liquid product on similar treatment.

Apiolaldehyde forms long, white needles, and melts at 75°. *Apiolic acid* crystallises in long, slender, white needles, melts at 151—152°, and is readily soluble in the ordinary solvents except water. *Apiolketonic acid* forms pale yellow plates, and melts at 175°.

The apioles from both sources are derived from the same apionol, $C_6H_2(OH)_4$. When the apiole from dill oil is fused with potash, it yields a *dimethylapionolcarboxylic acid*, a syrup which decomposes at 283° into carbonic anhydride and *dimethylapionol*, $C_6H_2(OH)_2(OMe)_2$, the *acetyl* derivative of which melts at 85°. Tetramethylapionol, $C_6H_2(OMe)_4$, melts at 89°, and not at 81° as previously stated (*Abstr.*, 1890, 36).

When the apiolic acid from dill oil is brominated, *dibromapione*, $C_6H_5Br_2O_4$, is obtained; it melts at 92°, and yields the corresponding *apion* on treatment with sodium ethoxide.

A. R. L.

Mercury Salts of Anilides. By HENRY L. WHEELER and B. W. McFARLAND (*Amer. Chem. J.*, 1896, **18**, 540—547).—*Mercury formanilide*, $\text{Hg}(\text{NPh}\cdot\text{CHO})_2$, is best prepared by dissolving formanilide and mercuric bromide in alcohol, adding the calculated quantity of sodium ethoxide, and diluting with water; it crystallises from water in colourless needles, and melts at about 194° . When it is suspended in benzene, and benzoic chloride (1 mol.) is added, it is converted into *chloromercury formanilide*, $\text{CHO}\cdot\text{NPh}\cdot\text{HgCl}$, which crystallises from water in lustrous, colourless plates, and melts at 191° . On concentrating the benzene solution, formylbenzanilide crystallises out, identical with the compound obtained from silver formanilide and benzoic chloride (this vol., i, 478). *Bromomercury formanilide* was prepared by suspending mercury formanilide in carbon bisulphide, and adding bromine (1 mol.) to the cooled liquid. *Iodomercury formanilide* was prepared in like manner. *Mercury formanilide acetate*, $\text{CHO}\cdot\text{NPh}\cdot\text{Hg}\cdot\text{OAc}$, crystallises in colourless, slender prisms when mercury acetate is mixed with formanilide in alcohol and the solution evaporated.

Mercury formoparatoluidide is prepared like the anilide; it crystallises from water in colourless needles; when treated with benzoic chloride, it yields *chloromercury formoparatoluidide*, which crystallises in colourless needles, and *formylbenzoparatoluidide*, which crystallises in colourless prisms, and melts at 101° .

Acetylbenzanilide is prepared in the same way as formylbenzanilide; it crystallises in long needles, and melts at 68° . *Mercury sym-tribrom-acetanilide*, $(\text{C}_6\text{H}_2\text{Br}_3\text{Nac})_2\text{Hg}$, crystallises from 50 per cent. alcohol in aggregates of needles. *Mercury formyl- α -naphthylamine*, $\text{Hg}[\text{N}(\text{C}_{10}\text{H}_7)\cdot\text{CHO}]_2$, crystallises in colourless needles.

The authors are of the opinion that the reaction of these mercury salts with benzoic chloride, resulting in the formation of a bi-acid anilide, is sufficient evidence to show that the mercury is united with the nitrogen of the anilide.

A. G. B.

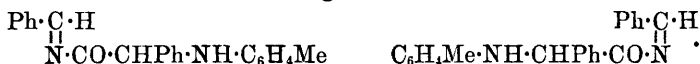
New Reactions and New Isomerides of Anil Compounds. By WILHELM VON MILLER and JOSEF PLÖCHL (*Ber.*, 1896, **29**, 1729—1741).—When benzylideneparatoluidine is heated in alcoholic solution with potassium cyanide, an acid of the formula



and two isomeric substances of the formula $\text{C}_{22}\text{H}_{20}\text{N}_2\text{O}$, are formed. The same two isomeric compounds are also obtained by the action of potassium cyanide on an alcoholic solution of benzylidenetoluidine and benzaldehyde, paratolilbenzoïn being also formed, and by the action of benzaldehyde on phenyltoluido-acetonitrile. One of these compounds crystallises in vitreous, monoclinic prisms, and melts at 197° . It is readily soluble in alcoholic potash, and combines with bromine to form an unstable compound. The isomeride crystallises in very small needles, melts at 261° , and is sparingly soluble in solvents of low boiling point. It is soluble with difficulty in alcoholic potash.

Each of these substances is converted by hot alcoholic potash

into a mixture of the two isomerides, whilst the substance melting at 197° is converted into the isomeride by heating above its melting point or by heating with alcoholic potassium cyanide. Both the compounds are hydrolysed by hydrochloric acid, with formation of benzaldehyde, ammonia, and phenyltoluidoacetic acid, which melts at 178 — 182° , and not at 167 — 170° as stated by Stoeckenius (*Jahresber.*, 1878, 779). The two compounds are, therefore, probably stereoisomeric, and have the following formulæ.



The acid product is also formed in small quantity by the action of potassium cyanide on benzaldehyde and benzyliidenetoluidine. It crystallises in small, soft prisms, and melts at 213° with evolution of carbonic anhydride. When heated with hydrochloric acid, it yields the same products as the two isomerides mentioned above. The *anhydride* forms silky needles, and melts at 215° . The *nitrile* is formed by the action of potassium cyanide on a mixture of phenyltoluidoacetoneitrile and benzaldehyde. It is a white, granular powder, and melts and decomposes at 262° .
A. H.

Behaviour of certain Diazo-compounds towards Potassium Sulphite. By EUGEN BAMBERGER and EMIL KRAUS (*Ber.*, 1896, 29, 1829—1835; compare von Pechmann, *Abstr.*, 1895, i, 370).—The solution of potassium sulphite employed in the authors' experiments was prepared by saturating with sulphurous anhydride a solution of caustic potash in 5 parts of water, and treating the liquid with potassium carbonate until strongly alkaline.

Paranitrodiazobenzene methyl ether, when agitated in ethereal solution with the potassium sulphite solution diluted with 10 parts of water, yields the *dipotassium* salt of paranitrophenylhydrazinedisulphonic acid, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{N}(\text{SO}_3\text{K}) \cdot \text{NH} \cdot \text{SO}_3\text{K}$, which separates in small, sulphur-yellow needles, and dissolves readily in hot water.

Paranitrophenylhydrazine, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{NH}_2$, is obtained in theoretical quantity on heating the foregoing salt with 18 per cent. hydrochloric acid on the water bath; it melts at 157° , and the *hydrochloride* crystallises in lustrous, brownish-red leaflets.

The action of potassium sulphite on potassium paranitroisodiazobenzene gives rise to the *dipotassium* and *tripotassium* salts of paranitrophenylhydrazinedisulphonic acid, which crystallises in flat, lustrous, ruby needles, and yields the *dipotassium* salt under the influence of carbonic anhydride; along with these substances, potassium paranitrophenyldiazosulphonate is produced. Paranitrodiazobenzene nitrate also yields the *dipotassium* salt, or potassium paranitrophenyldiazosulphonate, according to the conditions of the experiment; if an aqueous solution of the latter is rapidly cooled and vigorously agitated, lustrous, golden-yellow leaflets separate, consisting of an *isomeride*, which, when suspended in water, assumes the original form in the course of a day or two. The yellow modification is also produced when an aqueous solution of paranitrodiazobenzene nitrate at -2° is treated with the sulphite solution,

but the substance, even when washed with ice-cold water and preserved at low temperatures, becomes superficially brown, and acquires the odour of nitrobenzene and sulphurous anhydride; the dry product resinifies or explodes spontaneously. The labile modification is more readily soluble in water than the isomeric form, from which it differs, also, in the property of instantaneously developing colour with alkaline solutions of phenols; the aqueous solution decolorises potassium permanganate and iodine solutions.

The action of potassium sulphite on the potassium derivatives of normal and isodiazobenzene gives rise to potassium benzenediazo sulphonate.

M. O. F.

Aldehydates of Phenylhydrazine. By HENRI E. CAUSSE (*Compt. rend.*, 1896, **122**, 1274—1277).—Phenylhydrazine hydrogen tartrate is prepared in a crystalline form by dissolving 100 grams of tartaric acid in 500 c.c. of alcohol, adding 50 grams of phenylhydrazine and allowing the mixture to remain for 24 hours in a cool place. After separation and drying by pressure the crystals are washed with ether.

Acetaldehyde diphenylhydrazine, $\text{CMeHO}\cdot 2\text{N}_2\text{H}_3\text{Ph}$, is prepared by adding a solution of 10 grams of aldehyde in 90 grams of water to a solution of 50 grams of the hydrogen tartrate in 250 c.c. of water. It forms white, brilliant crystals which melt at $77\cdot 5^\circ$, and decompose and become yellow in contact with air. It also decomposes slowly in closed vessels. When distilled with dilute sulphuric acid, it yields aldehyde, and with barium hydroxide it yields phenylhydrazine.

Benzaldehyde diphenylhydrazine, $\text{C}_6\text{H}_5\cdot\text{CHO}\cdot 2\text{N}_2\text{H}_3\text{Ph}$, is obtained in a similar way, and crystallises from boiling alcohol in long, white needles which melt at 154° and becomes slightly yellow when exposed to air. When distilled with dilute sulphuric acid, it yields benzaldehyde and benzoic acid, and with barium hydroxide it yields phenylhydrazine.

C. H. B.

Constitution of Derivatives of Formic acid. By PAUL C. FREER and P. L. SHERMAN, jun. (*Amer. Chem. J.*, 1896, **18**, 562—584).—Formylphenylhydrazide was prepared by mixing 200 grams of phenylhydrazine with 200 grams of concentrated formic acid, and cooling the mixture. By dissolving it (59 grams) in a solution of sodium (10 grams) in absolute alcohol and pouring the solution into ether, *sodioformylphenylhydrazide*, $\text{N}_2\text{HPhNa}\cdot\text{CHO}$, is obtained in aggregates of felted needles after a short time. This compound decomposes rapidly in the air, aniline, phenylhydrazine, and sodium hydrogen carbonate being the chief products.

Ethylidene iodide and formylphenylhydrazide do not react in a sealed tube at 100° ; but when ethylidene iodide and sodium formylphenylhydrazine are mixed in alcoholic solution, the alcohol and excess of ethylidene iodide subsequently distilled off, and the residue poured into water, a heavy, colourless oil separates and solidifies on standing. This compound is *formylphenyl- α -ethylhydrazide*, $\text{NEtPh}\cdot\text{NH}\cdot\text{CHO}$, for, when reduced by sodium in amyl alcohol, it yields unsymmetrical phenylethylhydrazine, ethylaniline, and ammonia; it forms needle-shaped crystals, melts at $78\text{--}79^\circ$, and dissolves easily in all

organic solvents—except light petroleum; attempts to further ethylate it by means of ethylic iodide failed, but when it is heated under pressure at 100° with sodium ethoxide and ethylic iodide, *formylphenyldiethylhydrazide* is formed. This is a pale yellow, light oil, boiling at $139-140^{\circ}$ (5 mm. pressure); by reduction in the manner referred to above, it yields ethylamine and ethylaniline; alcoholic potash does not remove an ethyl group from it; neither phenylhydrazine nor sodium reacts with it.

When dry sodioformylphenylhydrazide is suspended in dry ether, and heated with ethylic iodide in a stoppered bottle at 100° , *formylphenyl- β -ethylhydrazide*, $\text{NHPh}\cdot\text{NEt}\cdot\text{CHO}$, is formed, which may be isolated by washing the ethereal solution with water, and drying and distilling it; the residual β -compound crystallises from alcohol in large rhombohedra, melts at 106° , and dissolves in all ordinary solvents, save light petroleum and water; much α -compound may be present in it if the sodium salt be not free from alcohol. The possible view that the compound is an imido-ether is negatived by its stability towards alkalis, and by the fact that it yields aniline and ethylamine by reduction such as has been described. The β -ethyl-derivative does not react with ethylic iodide and sodium ethoxide.

No evidence of the existence of a hydroxyl group in formylphenylhydrazide could be obtained by attacking the compound with acetic anhydride. The action of benzoic chloride and sodium ethoxide on formylphenylhydrazide leads to the formation of mono- and dibenzoylphenylhydrazide; the *sodium* derivative of the latter was prepared.

The behaviour of formanilide towards ethylic chlorocarbonate is shown to conform with that of silver formanilide to the same ethereal salt (compare Wheeler and Boltwood, this vol., i, 478). *Sodium formamide* and *silver formamide* are described. The action of sodium on ethylic formate yielded sodium ethoxide, carbonic oxide, and hydrogen as final products, but sodium ethylic formate appeared to exist as an intermediate compound, and a similar transitional existence of sodium amyllic formate was clearly indicated when amyllic formate was substituted for the ethylic salt.

The authors claim that the foregoing experimental work shows that in sodioformylphenylhydrazide the sodium is attached to nitrogen, and that, therefore, no hydroxyl group is present. There is no evidence of the presence of an aldehyde group, the existence of which in formic acid has been claimed by some, mainly because of the ease with which the acid is oxidised. In the salts of formanilide there is evidence of a hydroxyl grouping (compare Comstock and Kleeberg, *Abstr.*, 1890, 1414), but the authors hesitate to say the same of formanilide itself.

A. G. B.

Phenylhydrazones and Oxime of Protocatechuic Aldehyde.

By RUDOLF WEGSCHEIDER (*Monatsh.*, 1896, 17, 245—252).—This paper contains the details of the preparation of the above compounds, which have already been described (*Abstr.*, 1894, i, 79). The phenylhydrazone of higher melting point is designated the α -derivative, that of lower melting point being the β -form. Several cases of

isomerism among the aldehydephenylhydrazones are now known (compare this vol., i, 361). The oxime melts and decomposes at 149—151°.

A. G. B.

Action of Hydroxylamine on Nitrobenzene. By ANGELO ANGELI (*Ber.*, 1896, 29, 1884—1885).—Hydroxylamine reacts with nitrobenzene in alcoholic solution in presence of sodium ethoxide with formation of phenylnitrosohydroxylamine, $\text{NO} \cdot \text{NPh} \cdot \text{OH}$.

A. H.

Use of Antimony Trichloride in the Synthesis of Aromatic Ketones. By WILLIAM J. COMSTOCK (*Amer. Chem. J.*, 1896, 18, 547—552).—Antimony trichloride may be substituted for aluminium trichloride for the purpose of condensing any acid chloride of moderately high boiling point with an aromatic hydrocarbon. The mixture is heated in a reflux apparatus by means of a paraffin bath, the temperature being gradually raised to 200°. When no more gas is evolved, the mass is washed with strong hydrochloric acid in a separator to remove antimony; the ketone may then be dissolved in ether, and the solution dried by potassium carbonate and distilled. As an example of the method, the following recipe for the production of benzophenone is given:—Benzoic chloride 112 grams, benzene 70 grams, antimony trichloride 300 grams; with these proportions, the action is complete in about 12 hours. The application of the process to the formation of the tolyl phenyl ketones, and of paraxylyl ketone is also given. The yields are from 70 to 80 per cent. of the theoretical proportion.

A. G. B.

Halogen Substitution Products of Resacetophenone [2:4:1-Dihydroxyacetophenone] and of its Diethylic Ether. By R. SEGALLE (*Monatsh.*, 1896, 17, 314—326).—*Dichlorodihydroxyacetophenone* separates when chlorine is passed into an acetic acid solution of dihydroxyacetophenone; it forms white crystals, melts at 195—196°, and dissolves in ether, alcohol, glacial acetic acid, and benzene, but not in water. *Bromodihydroxyacetophenone* has not yet been prepared. *Diethylic dibromodihydroxyacetophenone ether* was prepared both by ethylating dibromodihydroxyacetophenone (*Abstr.*, 1894, i, 521) and by brominating diethylic dihydroxyacetophenone ether in carbon bisulphide; the product, however, is not the same. The α -ether, prepared by the first method, is white, melts at 51—52°, and dissolves in benzene, strong acetic acid and alcohol, but not in water. The β -ether crystallises in white needles, and melts at 127—129°. When bromination of diethylic dihydroxyacetophenone ether is conducted in acetic acid solution, *diethylic tribromodihydroxyacetophenone ether* is the chief product; it forms yellowish-white crystals, melts at 132—133°, and dissolves in alcohol and glacial acetic acid. *Tribromodihydroxyacetophenone*, prepared by brominating dihydroxyacetophenone in glacial acetic acid with excess of bromine, forms yellow crystals and melts at 112—113°. *Iododihydroxyacetophenone* crystallises in yellowish-white laminæ, and melts at 158—159°.

A. G. B.

Ethers of Unsaturated Hydroxy-ketones. By STANISLAUS VON KOSTANECKI and M. SCHNEIDER (*Ber.*, 1896, **29**, 1891—1894).—3-Ethoxybenzylidenacetophenone, $\text{OEt}\cdot\text{C}_6\text{H}_4\text{CH}:\text{CH}\cdot\text{COPh}$, crystallises from alcohol in yellowish prisms which melt at 75° , and form an orange-yellow solution in sulphuric acid.

4-Ethoxybenzylidenacetophenone forms yellowish, quadratic tablets melting at 63° , and also gives an orange-yellow solution in sulphuric acid.

Piperonalacetophenone, $\text{CH}_2\text{O}_2\cdot\text{C}_6\text{H}_3\cdot\text{CH}:\text{CH}\cdot\text{COPh}$, is formed by the condensation of piperonaldehyde with acetophenone, and crystallises in long, yellow needles melting at 122° .

5-Bromo-2-hydroxybenzylidenacetophenone,



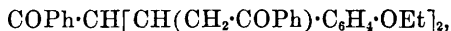
crystallises in yellowish prisms melting at 154 — 155° . It forms an orange coloured solution in sulphuric acid.

5-Bromo-2-acetoxybenzylidenacetone forms colourless prisms melting at 89 — 90° .

5-Bromo-2-benzoybenzylidenacetone, $\text{OBz}\cdot\text{C}_6\text{H}_3\text{Br}\cdot\text{CH}:\text{CH}\cdot\text{COMe}$, crystallises in prismatic needles melting at 123° .

5-Bromo-2-ethoxybenzylidenacetone crystallises in needles melting at 106 — 107° .

Di-2-ethoxybenzylidenetriacetophenone,



is obtained from 2-ethoxybenzaldehyde and acetophenone. It crystallises in needles, and melts at 190 — 192° .

The corresponding *meta*-compound melts at 225° , and the *para*-compound at 226 — 227° .

Dipiperonaltriacetophenone melts at 253 — 257° .

A. H.

Action of Methyl alcoholic Potash on 2 : 4 : 6-Trinitrobenzoic acid. By FREDERIK H. VAN LEENT (*Rec. Trav. Chim.*, 1896, **15**, 89—91; compare this vol., i, 147).—When a solution of trinitrobenzoic acid in methylic alcohol is treated with just sufficient caustic potash for neutralisation, a white precipitate of the potassium salt of the acid separates, if the solution is sufficiently concentrated. With an excess of alkali, a deep red precipitate is formed, but this varies in composition, and probably contains a considerable quantity of the colourless potassium salt. The red compound may be obtained in a pure form by adding to a boiling dilute solution of the acid in methylic alcohol (1.5 gram in 200 c.c.) the requisite quantity of alkali (2 mols. to 1 of acid). On cooling, brown-red crystals, having a strong metallic lustre, are deposited. These have the composition



A good yield of the same compound is obtained when the requisite quantity of potassium methoxide is added to a concentrated solution of the acid in absolute methylic alcohol. The crystals have a bitter taste, and explode when heated.

The authors state that the red solution obtained on adding an

excess of caustic potash solution to trinitrobenzoic acid contains potassium nitrite (compare V. Meyer, this vol., i, 419). After a lapse of several days, the above solution was acidified with hydrochloric acid, and extracted with ether; a reddish-brown oil was thus obtained, soluble in water, alcohol, and ether, but it could not be made to crystallise; it contains a strong *acid*, which gives rise to red *salts*. On boiling with barium carbonate, carbonic anhydride is evolved, and a gelatinous *barium* salt is formed. J. J. S.

3:4-Nitrohydroxybenzoic acid. By EMIL DIEPOLDER (*Ber.*, 1896, 29, 1756—1760).—3:4-Nitrohydroxybenzoic acid can be prepared by Barth's method, by the action of dilute nitric acid (1:6) on parahydroxybenzoic acid, and may be purified by means of the barium salt. 2:4-Dinitrophenol is formed in small quantity, together with the acid, particularly if the temperature is allowed to rise. The *ammonium* salt crystallises with water in long, bronze needles, melting and subliming at about 220°; the sublimate consists of small, yellow, rhombic crystals. Deninger's method for the preparation of the acid by the action of dilute sulphuric acid on a mixture of sodium nitrite and parahydroxybenzoic acid is inferior to Barth's dinitrophenol, being always formed in considerable quantity. 3:4-Amidoxybenzoic acid, formed by reduction of the nitro-acid by means of tin and hydrochloric acid, has been previously described; the *acetate* crystallises in flat rhombohedra, and when distilled, yields orthamidophenol.

When acted on by sodium nitrite and hydrochloric acid, the amido-acid yields a *diazoxide*, $\text{COOH} \cdot \text{C}_6\text{H}_3 < \overset{\text{O}}{\text{N}} > \text{N}$, which crystallises in yellow needles, darkens at about 110°, and explodes at 116—121°, according to the rapidity with which it is heated; it immediately becomes red when exposed to sunlight, dissolves in soda with a green and in sodium carbonate with a reddish-yellow coloration; dilute sulphuric acid added to the solutions gives rise to black and red flocculent precipitates respectively.

Amidophenoxazonecarboxylic acid, $\text{COOH} \cdot \text{C}_6\text{H}_3 < \overset{\text{N}}{\text{O}} > \text{C}_6\text{H}_2\text{O} \cdot \text{NH}_2$, is formed when the amido-acid is oxidised by means of potassium dichromate and dilute sulphuric acid; it is sparingly soluble and crystallises from ethylic benzoate in needles. The *ammonium* salt is pale red and flocculent, and its aqueous solution, when acidified with acetic acid, gives a dark red, flocculent precipitate, which is soluble in dilute sulphuric acid, showing that the oxazone is both an acid and a feeble base. The *calcium* salt crystallises with 5H₂O in small, dark red needles; the *barium* salt forms pale red, microscopic needles; the silver salt could not be prepared, as metallic silver is immediately deposited. The constitution of the oxazone is deduced from its analogy to the compound prepared by O. Fischer and O. Jonas by the oxidation of orthamidophenol; the absence of an imide or hydroxyl group is shown by the composition of the salts, and the monobasicity by titration. J. B. T.

Attempts to prepare Optically Active Parahydroxymethylbenzoic acids. By LEOPOLD RÜGHEIMER (*Ber.*, 1896, **29**, 1967—1969; compare V. Meyer and Heyl, this vol., i, 146).—The author describes experiments which indicate that, by means of the cinchonine salt, a modification of parahydroxymethylbenzoic acid may be obtained, the ammonium salt of which is laevorotatory.

M. O. F.

Constitution of Ethyl- β -resorcylic acid. By GEORG GREGOR (*Monatsh.*, 1896, **17**, 225—228; compare this vol., i, 171).—*Ethylic ethoxy- β -resorcyate* is obtained by heating an alcoholic solution of the potassium salt with ethylic iodide on the water bath; it crystallises from alcohol in long, colourless needles, and melts at 45°. It does not develop a coloration with ferric chloride, and is readily hydrolysed by potash.

M. O. F.

Action of Ethyloxalic Chloride [Ethylic Chloroglyoxylate] on Hydrocarbons of the Benzene Series in Presence of Aluminium Chloride. By LOUIS BOUVEAULT (*Compt. rend.*, 1896, **122**, 1207—1209; compare this vol., i, 551). Toluene and ethylic chloroglyoxylate yield *ethylic paracresylglyoxylate*, which is readily converted into *paracresylglyoxylic acid*. The latter, contrary to the statement of Roser, is a very stable substance, forms beautiful crystals which melt at 97°, and boils without decomposing at 164° under a pressure of 10 mm. When distilled under ordinary pressure, it splits up into a mixture of aldehyde and paratoluic acid.

Metaxylene yields *ethylic metaxylglyoxylate*, which boils at 165° under a pressure of 10 mm. without decomposing, and forms crystals which melt and partially decompose at 56°. The corresponding acid melts at 60°, and boils at 170° under a pressure of 10 mm.; it is readily converted into metaxylylcarboxylic acid melting at 125°.

Cymene (paraisopropyltoluene) yields *ethylic cymylglyoxylate*, which melts at 180°. Ethylcymene is formed at the same time, probably because ethylic chloride is produced by the action of the hydrogen chloride on the ethyloxalic chloride, and at the moment of its formation reacts with the cymene. Ethylcymene, however, cannot be obtained by the action of ethylic bromide on cymene in presence of aluminium chloride. *Cymylglyoxylic acid*, when distilled under ordinary pressure, yields aldehyde, a *cymenecarboxylic acid*, and a pale yellow oil, which boils at 220° under a pressure of 10 mm., and has the composition of cymophenone, $C_{10}H_{13} \cdot CO \cdot C_{10}H_{13}$. The latter is most probably produced by the action of heat on the cymylcarboxylic acid.

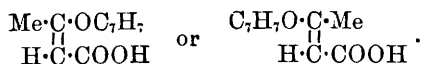
Anisoil yields *ethylic anisoylcarboxylate*, a pale yellow, oily liquid which boils at 183° under a pressure of 10 mm.

Anisoylcarboxylic acid, which has previously been obtained by the oxidation of anethoil, forms colourless needles which melt at 93°. When distilled it decomposes, and is converted into anisic acid, a very small quantity of anisaldehyde being also produced.

Veratrole, under similar conditions, yields *ethylic veratroylcarboxylate*; the acid, which forms colourless crystals melting at 135—136°, has already been obtained by the oxidation of methylisoeugenol.

When distilled in a vacuum, veratroylcarboxylic acid is entirely converted into veratric acid. C. H. B

Isomerism of the Crotonic acids. By WILHELM AUTENRIETH (*Ber.*, 1896, 29, 1639—1652).—When the sodium salts of β -chlorocrotonic acid and β -chlorisocrotonic acid are heated with sodium benzyloxide, one and the same β -benzyloxycrotonic acid is obtained; the structure of the latter compound is represented by one or other of the following formulæ.



It crystallises in slender, white needles, and melts sharply at 121.5 — 122° , decomposing at slightly higher temperatures into carbonic anhydride and β -benzyloxypropylene; it dissolves readily in alcohol, ether, and chloroform, but only sparingly in water; it is not affected by alkalis, but is completely decomposed by warm mineral acids, with the production of acetone, carbonic anhydride, and benzylic alcohol. The *potassium* salt crystallises in white, pearly leaflets.

β -Benzyloxypropylene, $\text{CH}_2 \cdot \text{CMe} \cdot \text{OC}_6\text{H}_5$, is a thick, colourless oil of agreeable odour, which distils at 191 — 192° without decomposing, and is volatile in steam; it decolorises bromine water, yielding a reddish oil.

If, in the above experiment, sodium benzyldisulphide is substituted for sodium benzyloxide, two isomeric thio-acids are obtained.

β -Thiobenzylisocrotonic acid, $\text{Me} \cdot \overset{\text{H}}{\underset{\text{H}}{\text{C}}} \cdot \text{SC}_6\text{H}_5$, is obtained, together with

benzylic bisulphide, when sodium β -chloroisocrotonate is heated in alcoholic solution with sodium benzyldisulphide. It may also be prepared by treating a mixture of ethylic acetoacetate and benzylic mercaptan with hydrogen chloride, and then shaking the product with water; the separated oil, ethylic β -dithiobenzylobutyrate, is heated with two molecular proportions of potash, and the resulting potassium salt decomposed by dilute sulphuric acid; the impure β -thiobenzylisocrotonic acid thus obtained is heated in a current of steam until benzylic bisulphide is no longer given off. It crystallises from dilute alcohol in beautiful prisms, and melts at 130 — 131° , decomposing at slightly higher temperatures into β -thiobenzyloxypropylene and carbonic anhydride. One part of the acid is dissolved by 30 parts of water at 15° . The *magnesium* salt forms beautiful tabular crystals; the *potassium* and *barium* salts are also described.

β -Thiobenzyloxypropylene, $\text{C}_6\text{H}_5 \cdot \text{S} \cdot \text{Me}$, when prepared from β -

chlorocrotonic acid in the above manner is accompanied by a large proportion of β -thiobenzylisocrotonic acid, the two being separable by means of alcohol, in which the latter is far more readily soluble. When, however, the sodium β -chlorocrotonate is shaken in the cold with sodium benzyldisulphide dissolved in alcohol, pure β -thiobenzyloxypropylene is obtained. It is insoluble in water, and is less readily soluble than the isomeric acid, both in alcohol and in ether; it dissolves

in 131 parts of water at 15° . When heated for a long time in sealed tubes at 130 — 160° , it is partially changed into its isomeride. Its salts crystallise well, those of *zinc* and *barium* forming pearly leaflets.

β -Thiobenzylpropylene, $\text{CH}_2\cdot\text{CMe}\cdot\text{S}\cdot\text{C}_7\text{H}_7$, is produced when either *β -thiobenzylcrotonic acid* is heated above its melting point. It forms a colourless oil with a disagreeable odour, and boils at about 225° . It is insoluble in water, but miscible in all proportions with alcohol and ether.

A. L.

Perhalogenised Phthalic acids and Hexiodobenzenes. By ERWIN RUPP (*Ber.*, 1896, 29, 1625—1634).—*Tetrabromoterephthalic acid*, $\text{C}_6\text{Br}_4(\text{COOH})_2$, is prepared by heating tetrabromoparaxylylene for eight hours in sealed tubes at 180° , with potassium permanganate and nitric acid. It crystallises in fine needles, melts and decomposes at 300° , dissolves in alcohol, ether, and acetic acid, but is only very sparingly soluble in cold water and benzene. It may also be prepared by Juvalta's process, namely, by heating terephthalic acid with bromine and fuming sulphuric acid in presence of a little iodine, first at 65° , and finally at 200° ; in this case it is accompanied by acids of lower halogen content, and by hexabromobenzene.

Tetrachloroparaxylylene, $\text{C}_6\text{Me}_2\text{Cl}_4$, is obtained by passing chlorine during three days through a solution of paraxylylene in chloroform containing iron dust in suspension; it crystallises from acetic acid in colourless, silky needles, melts at 218° , and dissolves readily in ether, benzene, and hot ethylic alcohol. When oxidised in the above manner, it yields *tetrachloroparatoluic acid*, $\text{C}_6\text{Cl}_4\text{Me}\cdot\text{COOH}$, which crystallises in needles, melts at 212° , and, when heated on the water bath with alkaline permanganate, yields *tetrachloroterephthalic acid*, $\text{C}_6\text{Cl}_4(\text{COOH})_2$. The latter dissolves in alcohol, acetic acid, and ether, but is insoluble in cold water and benzene; it crystallises in long, colourless prisms, and melts at 279 — 281° ; it is also formed from terephthalic acid by Juvalta's process.

Tetriadoterephthalic acid, $\text{C}_6\text{I}_4(\text{COOH})_2$, prepared from terephthalic acid by the foregoing method, forms colourless needles, melts and decomposes at 315 — 320° , and dissolves sparingly in acetic acid, ether, benzene, and boiling water. When prepared by Juvalta's process, it is accompanied by acids containing less iodine and by *hexiodobenzene*, C_6I_6 . The latter is insoluble in all the ordinary media, but may be crystallised from boiling nitrobenzene, when it is obtained as slender, brownish-red needles, which melt and decompose at 340 — 350° ; it is probable that Shaw (*Abstr.*, 1893, 14) was not dealing with this substance.

Tetrabromisophthalic acid, $\text{C}_6\text{Br}_4(\text{COOH})_2$, prepared from tetrabromometaxylylene or isophthalic acid, forms colourless needles, melts at 288 — 290° , and dissolves in ether, acetic acid, and methylic alcohol, but is insoluble in benzene and cold water. *Tetrachlorometatoluic acid*, $\text{C}_6\text{Cl}_4\text{Me}\cdot\text{COOH}$, prepared by oxidising tetrachlorometaxylylene, melts at 180 — 181° , and when heated with alkaline permanganate, yields *tetrachlorisophthalic acid*, $\text{C}_6\text{Cl}_4(\text{COOH})_2$, which forms slender, colourless needles, melting at 267 — 269° ; it dissolves readily in methylic

and ethylic alcohol, less readily in ether and acetic acid, and is insoluble in water and benzene. *Tetraiodisophthalic acid*,



crystallises in yellow prisms, melts and decomposes at 308—312°, and dissolves in methylic alcohol, but only sparingly in ether, acetic acid, or boiling water.

None of the foregoing substituted phthalic acids are etherified when heated with a 3 per cent. solution of hydrogen chloride in methylic alcohol.

Tetrabromophthalic anhydride is most readily obtained by Juvalta's process. When treated with methylic alcohol and hydrogen chloride, it yields a *monomethylic* salt; this separates from dilute alcohol in silky scales, sinters when heated, melts at 267°, and dissolves readily in benzene, ether and alcohol. *Tetriodophthalic anhydride*, $\text{C}_6\text{I}_4\langle\text{CO}\rangle\text{O}$, crystallises from acetic acid in lemon-yellow needles, melts at 320—325°, and is nearly insoluble in all ordinary solvents. *Tetriodophthalic acid*, $\text{C}_6\text{I}_4(\text{COOH})_2$, forms thick needles, melts at 324—327°, and is very sparingly soluble in acetic acid, alcohol, and ether. On etherification by Fisher's process, it yields a minute quantity of the dimethylic salt and a large proportion of *monomethylic salt*. The latter crystallises from acetic acid in sulphur-yellow, shining plates, melts and decomposes at 298°, and dissolves readily in alcohol, ether, and benzene. A. L.

Formation of Diphenylene Oxide from Phenylic Ether. By CARL GRAEBE and F. ULLMANN (*Ber.*, 1896, **29**, 1876—1877).—When orthamidophenylic ether (this vol., i, 605) is diazotised, it is converted into a diazo-compound, which is only decomposed very slowly by boiling water—rapidly by boiling 50 per cent. sulphuric acid, diphenylene oxide being formed. Diphenylene oxide is also formed when phenylic ether is passed through a glass tube heated to dull redness. A. H.

Preparation of Diphenacyl. By VICTOR FRITZ (*Ber.*, 1896, **29**, 1750—1751; compare this vol., i, 151).—Diphenacyl is best prepared by the action of magnesium powder on an alcoholic solution of bromodiphenacyl. The product contains a little bromine, and must be purified by recrystallisation, a 50 per cent. yield being obtained. A. H.

Condensation of Benzophenone Chloride with Benzene and Toluene : Tetraphenylethylene. By OTTO LOHSE (*Ber.*, 1896, **29**, 1789—1791).—After quoting Weisse's observation (this vol., i, 565) that triphenylcarbinol chloride does not condense with benzene, &c., in presence of aluminium chloride to form compounds of the type of tetraphenylmethane, and his own (*Diss. Griefswald*) that tetraphenylmethane derivatives are not present among the products of the action of benzophenone chloride, on benzene or toluene in presence of aluminium chloride, the author describes the following results.

When zinc dust is added in small portions to a mixture of benzo-

phenone chloride and a large excess of toluene, the products are tetraphenylethylene, and α - and β -benzopinacolines. If benzene is employed instead of toluene, the reaction is sluggish, and the yield of product small; the reaction may be rendered more brisk, however, by the addition of ether. Tetraphenylethylene may be prepared by the following method, without using metallic silver, as recommended by Behr (this Journal, 1872, 472). Copper-zinc dust, prepared by slowly adding zinc dust (2 mols.) to a slightly acid solution of copper sulphate, is introduced into an ethereal solution of benzophenone chloride, and subsequently a little ethereal hydrogen chloride is added. When the mixture is warmed in a reflux apparatus, a reaction sets in, and tetraphenylethylene is formed, together with the benzopinacolines. If the conditions are such as to preclude the formation of the benzopinacolines, the reaction proceeds very slowly.

A. R. L.

Menthene and Tertiary Menthol. By L. MASSON and ALBERT REYCHLER (*Ber.*, 1896, 29, 1843—1845).—Menthyl chloride prepared from *l*-menthol is added to a hot solution of potash in phenol, and heated for 12 minutes at 150°; on distilling the product, menthene is obtained.

When menthene is heated with trichloroacetic acid for half an hour at 70—90°, and the product agitated during 12 hours with potash, tertiary menthol (von Baeyer, *Abstr.*, 1893, i, 722) is produced.

M. O. F.

A Correction [Conversion of Pinene into Camphene]. By ALBERT REYCHLER (*Ber.*, 29, 1896, 1845—1846).—The author amends his view of the structural changes underlying the conversion of pinene into camphene (compare this vol., i, 313).

M. O. F.

Orientation in the Terpene Series. By ADOLF VON BAEYER (*Ber.*, 1896, 29, 1907—1922; compare this vol., i, 245 and 308).—Pinic acid is shown to contain the group $\text{—CH}_2\text{—COOH}$ by bromination, conversion of the bromo-acid into hydroxypinic acid (this vol., i, 308), elimination of carbonic anhydride, and oxidation of the aldehyde produced to norpic acid.

Bromopinic acid, $\text{COOH}\cdot\text{CH}\langle\begin{smallmatrix} \text{CMe}_2 \\ \text{CH}_2- \end{smallmatrix}\rangle\text{CH}\cdot\text{CHBr}\cdot\text{COOH}$, is obtained by treating pinic acid with phosphorus tribromide and bromine; the product is thrown into boiling water and extracted with ether, the solvent depositing an oil, from which crystals gradually separate. Hydroxypinic acid (*loc. cit.*) is prepared from it by the action of barium hydroxide; copper acetate, which causes no precipitate in a cold solution, produces in the hot liquid a turbidity, which disappears on cooling.

Norpic acid aldehyde, $\text{COOH}\cdot\text{CH}\langle\begin{smallmatrix} \text{CMe} \\ \text{CH}_2- \end{smallmatrix}\rangle\text{CH}\cdot\text{COH}$, is formed on adding lead peroxide in small portions to a hot solution of hydroxypinic acid in dilute acetic acid, and is obtained as an oil, which dissolves readily in water, but exhibits no tendency to deposit crystals; the semicarbazone, $\text{C}_9\text{H}_{15}\text{N}_3\text{O}_3$, crystallises from hot water in plates,

and melts, evolving gas, at 188—189°. The aldehyde gives a metallic mirror with an ammoniacal silver solution, and treatment of the oxime with acetic anhydride, gives rise to a nitrile.

Norpic acid, $\text{COOH}\cdot\text{CH}\langle\begin{smallmatrix}\text{CMe}_2 \\ \text{CH}_2\end{smallmatrix}\rangle\text{CH}\cdot\text{COOH}$, is obtained by oxidising the foregoing aldehyde in alkaline solution with a 4 per cent. solution of potassium permanganate; it separates from ether in large, prismatic crystals, and melts at 173—175°, subliming about 100° in needles. The substance is probably identical with the acid $\text{C}_8\text{H}_{12}\text{O}_4$, obtained by Wagner and Ertschikowsky, on treating pinonic acid with alkali hypobromite (this vol., i, 380). In its behaviour towards copper acetate, norpic acid resembles pinic acid, whereas the α -pinonic acid yields bluish-green needles on warming the moderately concentrated solution; the *silver* salt crystallises in needles. Boiling acetic chloride does not convert norpic acid into an anhydride, and its stability towards oxidising agents is as marked as that of pinic acid.

When pinene is oxidised under slightly modified conditions, there is produced along with α -pinonic acid a dibasic ketonic acid, derived from the monobasic acid by oxidation of the methylic group attached to the carbonyl radicle; it is named pinoylformic acid, and yields pinic acid on oxidation, whilst hot dilute sulphuric acid converts it into a lactonic acid, bearing to the lactonic isomeride of α -pinonic acid the relation in which an α -ketonic acid stands to a methyl ketone.

Pinoylformic acid, $\text{COOH}\cdot\text{CH}_2\cdot\text{CH}\langle\begin{smallmatrix}\text{CMe}_2 \\ \text{CH}_2\end{smallmatrix}\rangle\text{CH}\cdot\text{CO}\cdot\text{COOH}$, is separated from the mixture containing α -pinonic acid by adding potassium carbonate in quantity insufficient to neutralise the latter acid, which is then removed by extraction with ether; the alkaline liquid containing potassium pinoylformate is acidified, and agitated with ether, the oil obtained on evaporating the solvent being then treated with potassium hydrogen sulphite, and the pinoylformic acid liberated from the resulting compound by means of concentrated barium hydroxide. It is more readily soluble than α -pinonic acid in cold water, and crystallises in thin leaflets, which melt at 78—80°; the *silver* salt crystallises in beautiful, lustrous leaflets, which resist the action of light, but copper acetate produces no precipitate in hot or cold solutions of the acid, cuprous oxide being precipitated only when the liquid is boiled for a long time. The *potassium hydrogen sulphite* compound crystallises very readily in aggregates of needles, and the *sodium hydrogen sulphite* compound, which is more soluble in cold water, separates in white leaflets; the *phenylhydrazone* crystallises in flat prisms, and melts, evolving gas at 192.5°. As already stated, oxidising agents convert pinoylformic acid into pinic acid; fuming nitric acid gives rise to oxalic and terpenylic acids.

Homoterpenoylformic acid, $\text{CO}\cdot\text{CH}_2\langle\begin{smallmatrix}\text{O}\cdot\text{CMe}_2 \\ \text{CO}\cdot\text{CH}_2\end{smallmatrix}\rangle\text{CH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}\cdot\text{COOH}$, is obtained by treating pinoylformic acid with hot, 10 per cent. sulphuric acid; it is sparingly soluble in ether and cold water, and crystallises in prisms, melting at 126—129°. The production of this sub-

stance is parallel with the conversion of α -pinonic acid into homoterpenylic methyl ketone (methylethylheptanonolide). On titration with decinormal alkali, homoterpenoylformic acid behaves as a monobasic acid, and the same observation applies to pinoylformic acid; as however, the phenylhydrazone of the latter is dibasic, it is probable that free pinoylformic acid is an acid lactone, the oxygen ring of which is ruptured by phenylhydrazine. Homoterpenoylformic acid resembles pinoylformic acid in behaviour towards copper acetate, but silver nitrate gives no precipitate; the *oxime* crystallises in slender needles, and melts at about 170° , when vigorous liberation of gas occurs.

Homoterpenylic acid, $\begin{matrix} \text{O} \cdot \text{CMe}_2 \\ | \\ \text{CO} \cdot \text{CH}_2 \end{matrix} > \text{CH} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{COOH}$, is obtained from homoterpenoylformic acid alike by lead peroxide and fuming nitric acid; it dissolves somewhat sparingly in cold water, and crystallises in large, lustrous prisms, melting at $98-101^{\circ}$. Ether dissolves it with difficulty, and the crystals from this solvent melt at $100-102.5^{\circ}$. Homoterpenylic acid has to adipic acid the same relation as that in which terpenylic and terebic acids stand to glutaric and succinic acids respectively; it is noteworthy that the relative fusibility observed in the succinic series is reproduced amongst the lactonic derivatives.

M. O. F.

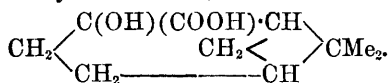
Orientation in the Terpene Series. Nopic acid. By ADOLF VON BAEYER [and VICTOR VILLIGER] (*Ber.*, **29**, 1896, 1923—1929).—Nopic acid is the acidic product of oxidation of French turpentine oil, and is isomeric with α -pinonic acid, but contains no ketonic group (this vol., i, 247). It dissolves with difficulty in water, crystallising from it in long needles, which melt at $126-128^{\circ}$; the sodium salt crystallises in lustrous, rectangular leaflets, and the *potassium* salt, which is more readily soluble in water, resembles it closely. The *barium* and *calcium* salts crystallise in long, slender prisms, and the *silver* salt, which dissolves with extreme difficulty in cold water, forms needles, which resist the action of light; the *copper*, *zinc*, *cadmium*, *manganese*, and *lead* salts are also crystalline.

Bromotetrahydrocuminic acid, $\text{CHMe}_2 \cdot \text{C} \begin{matrix} \text{CH}_2 \cdot \text{CH}_2 \\ \text{CH} \cdot \text{CH}_2 \end{matrix} > \text{CBr} \cdot \text{COOH}$, is obtained by the action of hydrogen bromide on nopic acid dissolved in glacial acetic acid; it is soluble in chloroform, dissolves sparingly in ether, and is insoluble in petroleum, crystallising in lustrous, rhombic leaflets, which melt, evolving gas at 175° . It decolorises potassium permanganate, and yields silver bromide when treated with boiling aqueous silver nitrate.

Dihydrocuminic acid is produced by the action of hot, 25 per cent. sulphuric acid on the foregoing substance, which yields the same product under the influence of alcoholic potash; it separates from alcohol in prismatic crystals, and melts at $130-133^{\circ}$. It sublimes at about 100° , and boils at 176° under a pressure of 14 mm.; it dissolves with extreme difficulty in water, but the *sodium* salt is readily soluble, and the *silver* salt crystallises in small needles. The substance reduces a cold, alkaline solution of potassium permanganate, and is oxidised to cuminic acid by potassium ferrieyanide.

Nopinone, $\text{CH}_2 \begin{array}{c} \text{CO} \text{---} \text{CH} \\ \text{CH}_2 \text{---} \text{CH} \\ \text{CH}_2 \text{---} \text{CH} \end{array} \text{CMe}_2$, is obtained on passing a current

of steam through water in which nopic acid and lead peroxide are suspended; it is a volatile oil of refreshing odour, and is converted by hot, dilute sulphuric acid into a ketone, which is readily oxidised by potassium permanganate. The *oxime* is an oil, and the *semicarbazone* crystallises from methylic alcohol in slender needles, melting at 188.5° . Fuming nitric acid oxidises nopinone, forming homoterpenylic acid, and from this change is deduced the above expression for the constitution of the ketone; the structure of nopic acid is therefore represented by the formula,



M. O. F.

Anemonin. By HANS MEYER (*Monatsh.*, 1896, **17**, 283—299).—Crystallographical measurements of anemonin are given, and our present knowledge of the compound, deducible from this paper and that of Beckurts (*Abstr.*, 1892, 1241) is summarised as follows:—(1) Its formula is $\text{C}_{10}\text{H}_8\text{O}_4$. (2) It yields methyl and ethyl derivatives, which are apparently ethereal salts, showing that it is the anhydride of a dicarboxylic acid. *Dimethylanemonin*, $\text{C}_8\text{H}_8(\text{COOMe})_2$, melts at $109\text{--}110^\circ$, *methylanemonin* at $174\text{--}176^\circ$, *diethylanemonin* at 47° , and *ethylanemonin* at $168\text{--}170^\circ$. (3) The said dicarboxylic acid is a ketonic acid (*loc. cit.*). (4) By oxidation, anemonin yields succinic and oxalic acids. (5) By hydrolysis of the dialkyl salts before mentioned with alkali and amorphous acid, $\text{C}_{10}\text{H}_8\text{O}_4 + 2\text{H}_2\text{O}$ is formed, but hydrolysis of them with hydrochloric acid yields a crystalline acid, $\text{C}_{10}\text{H}_8\text{O}_4 + \text{H}_2\text{O}$ (compare Beckurts, *loc. cit.*). The amorphous acid gives coloured, the crystalline acid colourless, salts. (6) Anemonin is a saturated compound, for by reduction it yields a saturated hydroxy-acid, and absorbs neither chlorine (Hübl solution) nor bromine.

The paper concludes with a discussion of the relative position of the carbonyl to the carboxyl group in anemonin. A. G. B.

Columbin and Columbic acid. By ALBERT HILGER (*J. Pharm.*, 1896 [6], **3**, 299—300; from *Apoth. Zeit.*, 1896, 73).—Columbo roots, in a suitable state of division, are extracted several times with boiling ether. During the cooling, columbin, slightly coloured and contaminated by small quantities of oily matter and of cholesterol, separates. It is merely necessary to wash with cold alcohol and to recrystallise in order to obtain the pure columbin.

The roots are then extracted with 90 per cent. boiling alcohol and finally boiled with dilute milk of lime. The latter extract is filtered, and the filtrate decomposed by means of hydrochloric acid, when columbic acid, mixed with a little berberine and columbin, separates. The acid is best purified by first washing with water until the washings cease to give the reactions for berberine, and finally with boiling ether to remove the columbin.

Columbin, $C_{21}H_{24}O_7$, forms colourless needles, is insoluble in hot and cold water, also in cold alcohol or cold ether, but is readily soluble in boiling ether, chloroform, or alcohol. It melts at 182° , and, when treated with hydrochloric acid, is converted into a monobasic acid, $C_{21}H_{24}O_7$. The same acid is formed when columbin is treated with cold dilute alkalis or with hydrobromic or hydriodic acid.

Columbic acid is a yellow amorphous powder, which, after a time, turns brown. It has the characteristic odour of columba root, and is insoluble in water and ether, but readily soluble in cold alcohol. An ammoniacal solution of silver nitrate is reduced in the cold by the acid. It is a monobasic acid, and contains one methoxy-group.

J. J. S.

Chlorophyll. By W. A. ALEXANDER TSCHIRCH (*Ber.*, 1896, **29**, 1766—1770).—A reply to Schunck and Marchlewski's criticisms (this vol., i, 574) of the author's previous paper on this subject. All chlorophyll derivatives hitherto examined show an absorption band at H, and this is identical with Soret's blood absorption band in the violet. The purity of the phyllocyanic acid is shown by analysis of three different specimens; no fatty acids could be detected. Phylloporpuric acid is also homogeneous when prepared by the author's method, which consists in fusing "alkali-chlorophyll" with potash at 210° , dissolving the residue in water, acidifying with hydrochloric acid, and extracting the solution with ether; under these circumstances the ether dissolves only the compound in question, which can readily be obtained in crystals. Schunck and Marchlewski's compound, and that of Hoppe-Seyler, may or may not be identical with this. The fact that phylloxanthin is readily converted into phyllocyanin is no proof that the former is first formed in the leaf extract; the quantity present in solution increases spontaneously if the liquid is kept, and it appears that the reverse change occasionally takes place. The positions of the absorption bands of phylloporpuric acid and hæmatoporphyrin (two specimens) are fully tabulated according to the author's observations.

J. B. T.

Stereoisomeric Copellidines. II. By LUDWIG LEVY and RICHARD WOLFFENSTEIN (*Ber.* 1896, **29**, 1959—1960; compare *Abstr.*, 1895, i, 683).—Copellidine and isocopellidine are separated from each other by treating the mixed hydrochlorides with acetone, which leaves pure copellidine hydrochloride undissolved; the crystalline mixture obtained on evaporating the acetone is spread on porous earthenware, when isocopellidine hydrochloride deliquesces, and may be extracted with acetone after removing the isomeride, which remains on the surface of the plate.

A table included in the paper gives the boiling point, specific gravity, and specific rotatory power of the six stereoisomeric copellidines, along with the melting point of the principal salts.

The authors attribute the isomerism of the copellidines to the relative position, *cis* or *trans*, of the methyl and ethyl groups.

M. O. F.

An Indolium Base and its Indolinone. By KARL BRUNNER (*Monatsh.*, 1896, 17, 253—281; compare this vol., i, 169).—*Isobutylidenephénylmethylhydrazine*, $C_{11}H_{16}N_2$, prepared from isobutaldehyde and phenylmethylhydrazine, was found to be a colourless liquid distilling at $160\text{--}163^\circ$ (48 mm.). In the hope of obtaining a homologue of the hypothetical base $C_{10}H_{11}N$ (*loc. cit.*), this phenylhydrazine was mixed with an alcoholic solution of zinc chloride in an atmosphere of carbonic anhydride, and after five days ether was added; the yellow crystalline powder which separated was treated with potash and shaken with ether; on evaporation of the solvent,

1' : 3' : 3'-trimethylindolium hydroxide, $C_6H_4 < \begin{smallmatrix} CMe_2 \\ NMe(OH) \end{smallmatrix} > CH$, was

left; this crystallises in colourless, microscopic prisms, melts at 95° , and is very soluble in alcohol, ether, and benzene, less so in light petroleum and in boiling water; it has an odour of thymol and excites sneezing; it volatilises with steam. With a hydrochloric acid solution of the base, ferric chloride gives a yellow precipitate, soluble in alcohol and water. With strong sulphuric acid and a granule of potassium dichromate, it yields an intense brown coloration, which is red if the base has become yellow from exposure to air. The base is a powerful reducing agent. The *hydrochloride* melts at 131° ; the *sulphate*, $C_{11}H_{14}N \cdot HSO_4 + H_2O$, melts, when anhydrous, at 129° ; the *mercurochloride* melts at 125° , and the *platinochloride* at 161° . The base and its salts are toxic and alkaloidal in character; the physiological effects are detailed. When boiled with strong hydrochloric acid, the base is converted into Degen's trimethylindole (*Abstr.*, 1887, 149), which melts at 18° and boils at $283\text{--}284^\circ$ (750 mm.). Nitration of the base produces the *dinitro-derivative*, $C_{11}H_{11}(NO_2)_2NO$, which forms yellow crystals and melts at 148° ; bromination produces the *tribromo-derivative*, $C_{11}H_{11}Br_2NO$, which crystallises in colourless needles and melts at 126° ; reduction with zinc dust produces a crystalline substance, which melts at 129° and has the empirical formula $C_{11}H_{14}N$, but is supposed from its indifferent character to be a bimolecular form, $(C_{11}H_{14}N)_2$.

1' : 3' : 3'-Trimethyl-2'-indolinone, $C_6H_4 < \begin{smallmatrix} CMe_2 \\ NMe \end{smallmatrix} > C:O$, is prepared by oxidising the indolium hydroxide by boiling its alcoholic solution with an ammoniacal alcoholic solution of silver nitrate; after filtering from the silver and distilling off the alcohol, the oxidation product may be extracted by ether. At first a colourless oil, boiling at $264\text{--}265^\circ$ (751 mm.), it solidifies at low temperatures to crystals which melt at 25° , but if kept at ordinary temperatures these crystals undergo a change and melt at 50° . It has an odour of peppermint, dissolves in organic solvents, and is easily volatile with steam; the *platinochloride*, with $1\frac{1}{2}H_2O$, the *aurochloride*, and the *mercurochloride* (m. p. $122\text{--}123^\circ$) are described. By bromination, the indolinone yields the same bromine derivative, $C_{11}H_{11}Br_2NO$, as is obtained from the indolium base. By nitration, a *mononitro-derivative*, $C_{11}H_{12}NO \cdot NO_2$, is first formed; this melts at $201\text{--}202^\circ$, and, when further nitrated, passes into the same dinitro-compound as was obtained from the

indolium base. It thus seems that the indolium base is first converted into the indolinone by both bromine and nitric acid.

A. G. B.

Ethylic Quinate and its Conversion into Dihydroxyquinoline. By FRIEDRICH HIRSCH (*Monatsh.*, 1896, **17**, 327—342).—*Ethylic quinate*, prepared by passing hydrogen chloride into an alcoholic solution of quinic acid, crystallises in colourless needles, melts at 69° (uncorr.), and is insoluble in water; its *hydrochloride* melts at 160° (uncorr.); the *platinochloride* (with 2H₂O) is described. *Quininamide* crystallises in long, silky, colourless needles, melts at 197°, and dissolves freely in alcohol, sparingly in water and ether, and not at all in benzene and light petroleum; the *hydrochloride* and *platinochloride* are described.

When the amide is treated with potassium hypobromite, it is converted into 3 : 4'-*methoxyamidoquinoline* which crystallises in white needles, and melts at 120°; the *hydrochloride* partly decomposes and melts at 249°, the *platinochloride* at 230°. Through the diazo-reaction, the corresponding 3 : 4'-*methoxychloroquinoline* was prepared; it crystallises in small, colourless, lustrous needles, and melts at 76·5° (uncorr.); the *hydrochloride* melts at 191°, and the *aurochloride* at 177° (uncorr.). The methoxychloroquinoline can be converted into the corresponding *dimethoxyquinoline* by sodium methoxide at 140°, and this into 3 : 4'-*dihydroxyquinoline* by hydrochloric acid at 190°, the latter and its *aurochloride* decompose before they melt. Eleven of the 21 possible dihydroxyquinolines are now known.

A. G. B.

Hydroxytheophyllin. By OSKAR WIDMAN (*Ber.*, 1896, **29**, 1954—1956).—The ready conversion of α -acidyl derivatives of phenylsemicarbazide into substituted 3 : 1-hydroxyphenyltriazoles under the influence of dilute alkali, suggested the possibility of obtaining xanthine by this means from hydroxyxanthine. The only result of the action, however, is liberation of ammonia, and production of amidouracil, and a similar experiment with hydroxytheophyllin, the dimethyl derivative of hydroxyxanthine, gave rise to amidodimethyluracil. This method of condensation, therefore, is inapplicable to the compounds in question.

Hydroxytheophyllin, $\text{CO} < \begin{smallmatrix} \text{NMe} \cdot \text{CH} \\ \text{NMe} \cdot \text{CO} \end{smallmatrix} > \text{C} \cdot \text{NH} \cdot \text{CO} \cdot \text{NH}_2$, is obtained by heating hydroxyxanthine with methylic iodide and sodium methoxide for eight hours at 130—140°; it crystallises from water in small, four sided plates, and when heated evolves gas, but does not melt below 290°. It is insoluble in cold hydrochloric acid, and when evaporated with nitric acid yields a carmine-red residue, which develops a violet coloration with ammonia. When heated with concentrated ammonia for an hour and a half at 140°, it yields a compound which crystallises from alcohol in needles, and melts at 163°; in behaviour towards nitric acid it resembles hydroxytheophyllin.

M. O. F.

Lophine and Glyoxalines. By VICTOR KULISCH (*Monatsh.*, 1896, **17**, 300—308).—In view of Radziszewski's synthesis of lophine and of the formula which he interprets therefrom (*Abstr.*, 1882,

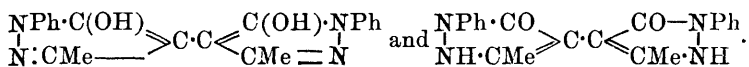
1063), it seemed probable that benzamidine and benzoin should condense to form an isomeride of lophine. The author finds, however, that lophine itself is the product of the condensation. Ethyllophine (m. p. 234°) yields ethylamine when heated with alcoholic potash, showing that the ethyl group is attached to nitrogen, a conclusion which is confirmed by treating ethyllophine by Herzig and Meyer's method (Abstr., 1895, ii, 296). The same method also showed the presence of ethyl attached to nitrogen in ethylglyoxaline, so that the author concludes that Japp's formula for lophine (Trans., 1882, 323), is correct, and that Radziszewski's formula must be rejected.

A. G. B.

Action of Phenylhydrazine on the Isomeric Ethylic β -Chlorocrotonates. By WILHELM AUTENRIETH (*Ber.*, 1896, 29, 1653—1664).—*Ethylic β -chlorisocrotonate* is readily prepared by the action of ethylic alcohol and hydrogen chloride on the corresponding acid. It is a colourless oil of an agreeable odour, and boils at 157—158° under 740 mm. pressure. *Ethylic β -chlorocrotonate*, when prepared in the above manner is obtained unaccompanied by the isomeric salt, and distils at 179—180°.

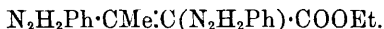
Phenylhydrazine and either of the foregoing ethylic salts interact at 100° with production of a mixture of substances; this is extracted with ether, which leaves undissolved bis-phenylmethylpyrazolone and phenylhydrazine hydrochloride, whilst the ethereal solution, on evaporation, deposits a mixture of 1 : 3 : 5-phenylmethylpyrazolone, phenylmethylpyrazoloneazobenzene, and the excess of phenylhydrazine.

The above bis-phenylmethylpyrazolone is identical with that described by Knorr (Abstr., 1884, 1379), the statements extant that this substance is insoluble in alcohol and ammonia being erroneous. When treated with acetic anhydride, it yields but one *diacetyl* derivative, $C_{24}H_{22}N_4O_4$. This crystallises from dilute alcohol in slender needles, dissolves somewhat readily in alcohol, ether, and chloroform, but is insoluble in water; it is not attacked by a boiling solution of sodium carbonate, but is hydrolysed by concentrated potash; it melts at 132—134°. The *dibenzoyl* derivative, $C_{34}H_{26}N_4O_4$, is readily soluble in alcohol, ether, and chloroform, but is not dissolved by water; it crystallises from alcohol in fine needles, and melts at 189—190°. The *disulphonyl* compound, $C_{32}H_{26}N_4S_2O_6$, prepared by adding to a hot alkaline solution of the substance a quantity of benzenesulphonic chloride, crystallises from alcohol in needles, and melts at 190°; it is readily soluble in ether and hot alcohol, sparingly in cold alcohol, and insoluble in water. The production of the foregoing compounds leads the author to propose for bisphenylmethylpyrazolone, the tautomeric formulæ—



The "azo" compound above mentioned is identical with Knorr's 1-phenyl-3-methyl-4-azobenzene, prepared by the interaction of phenylmethylpyrazolone and diazobenzene chloride (Abstr., 1887,

602), and also with the substance obtained by that author (Abstr., 1887, 603) by acting on rubazonic acid with phenylhydrazine. Its production by the interaction of ethylic β -chlorocrotonate and phenylhydrazine is most probably preceded by the formation of ethylic $\alpha\beta$ -diphenylhydrazidocrotonate,



The product, obtained when this substance is treated with nitric acid in the manner described by Knorr (*loc. cit.*), is a mixture of a mononitro- and a dinitro-derivative, which may be separated by means of alcohol. The *mononitro*-derivative, $\text{C}_{16}\text{H}_{13}\text{N}_5\text{O}_3$, which is of an orange colour, melts and decomposes at about 234° , is somewhat readily soluble in hot alcohol and chloroform, but is insoluble in water. The *dinitro*-compound, $\text{C}_{16}\text{H}_{12}\text{N}_6\text{O}_5$, is of a bright yellow hue, melts and decomposes at 292 – 294° , and is insoluble in water, alcohol, and ether, but dissolves readily in chloroform. A. L.

Marcourt's "Formopyrine." By FRIEDRICH STOLZ (*Ber.*, 1896, 29, 1826—1828).—The substance obtained by Marcourt (*Bull. Soc. Chim.*, 1896, 13, 520) on allowing antipyrine and formaldehyde to remain together in solution, is identical with methylenedianitipyrine (Abstr., 1895, i, 482). This is established by crystallographic comparison of the two compounds, which have the same molecular weight. Pellizzari has quite recently arrived at the same conclusion.

M. O. F.

Formation of Phenazine. By OTTO FISCHER (*Ber.*, 1896, 29, 1873—1876; compare Abstr., 1893, i, 266).—The synthesis of phenazine derivatives by the action of lead peroxide on amido-compounds succeeds in a large number of cases.

Orthamidophenyltolylamine is obtained by the reduction of the corresponding nitro-compound, and crystallises in tablets melting at 76 – 77° . When its vapour is passed over heated lead peroxide, toluphenazine, melting at 117° is formed. When diamidodiphenylamine [$\text{NH} : (\text{NH}_2)_2 = 1 : 2 : 4$] is heated with lead peroxide it is at once converted into amidophenazine, although Nietzki and Bauer (this vol., i, 164) were unable to convert this amido-compound into the phenazine derivative.

Dinitroparamethoxydiphenylamine is obtained by the action of bromodinitrobenzene on paranisidine. It forms large, pointed, scarlet crystals melting at 141° . On reduction, it yields *diamidoparamethoxydiphenylamine*, which crystallises in colourless tablets melting at 118 – 120° , and becomes coloured violet on exposure to air. When heated with lead peroxide, it is converted into sym-*paramidomethoxyphenazine*, $\text{NH}_2\cdot\text{C}_6\text{H}_3\cdot\begin{smallmatrix} \text{N} \\ \diagup \quad \diagdown \\ \text{N} \end{smallmatrix}\cdot\text{C}_6\text{H}_3\cdot\text{OMe}$, which crystallises in reddish-yellow needles melting at 216 – 217° . A. H.

Constitution of the Safranines. By OTTO FISCHER (*Ber.*, 1896, 29, 1870—1873).—The azonium theory of the constitution of the safranines has been supported by Nietzki (this vol., i, 580), on the ground of the great basicity of many of the compounds in question

The author finds that aposafranine hydrochloride, diacetylphenosafranine hydrochloride, and acetylposafranine hydrochloride are all decomposed in dilute solution by dilute soda, the last compound being also decomposed by sodium acetate. The basicity even of true quaternary ammonium bases seems to depend not only on the constitution but also on the other properties of the substance. Thus the products of the action of benzil, β -naphthaquinone and phenanthraquinone on orthamidodiphenylamine and of β -naphthaquinone on orthamidoditolylamine are all decomposed by dilute sodium carbonate. A further objection to Nietzki's formula is that it requires the elimination of water between an amido- and an ammonium hydroxide group in the meta-position.

A. H.

Synthesis of Aposafranone (Benzeneindone). By FRIEDRICH KEHRMANN and H. BÜRGIN (*Ber.*, 1896, **29**, 1819—1820).—When metadinitrophenylorthamidodiphenylamine (Abstr., 1893, i, 199) is heated with benzoic acid until nitric oxide is no longer liberated, *aposafranone*, or benzeneindone (Abstr., 1895, i, 528) is produced; the same substance was originally obtained by Kehrmann and Messinger on heating the foregoing diphenylamine derivative with benzil. It crystallises in lustrous, green needles, and melts at 248—249°; mineral acids give rise to well-defined salts, the hydrochloride forming reddish-brown crystals, but acetic acid does not combine with it. The solution in concentrated sulphuric acid appears green when examined in thin layers, and is purple-red under ordinary conditions.

This method of synthesising aposafranone is further evidence in support of the phenosafranine formula, $O\cdot C_6H_3\cdot \begin{smallmatrix} N \\ \diagup \quad \diagdown \\ NPH \end{smallmatrix} > C_6H_4$, already adopted.

M. O. F.

A Group of 3:1-Hydroxyphenyltriazoles. By OSKAR WIDMAN (*Ber.*, 1896, **29**, 1946—1953).—The production of 3:1-hydroxyphenyltriazole by treating phenylsemicarbazide with boiling formic acid (Abstr., 1894, i, 57) has been followed by the observation that α -acidyl derivatives of phenylsemicarbazide are converted into substituted hydroxyphenyltriazoles under the influence of 10 per cent. potash at 50°. The compounds thus obtained are distinctly acidic, and also form hydrochlorides, but no platinochlorides; they do not reduce Fehling's solution.

α -Acetophenylsemicarbazide, $NPh\cdot Ac\cdot NH\cdot CO\cdot NH_2$, is prepared from phenylsemicarbazide and acetic chloride dissolved in benzene; it crystallises from alcohol in leaflets, and melts at 196—197°, evolving ammonia. α -Chloracetophenylsemicarbazide crystallises in flat needles and melts at 182°.

Phenylglycinyphenylsemicarbazide,



is obtained from the foregoing compound and aniline, and melts at 202°. *Propionylphenylsemicarbazide*, $CH_3Me\cdot CO\cdot NPh\cdot NH\cdot CO\cdot NH_2$, crystallises in needles, and melts, evolving gas, at 185—186°.

3 : 1 : 5-*Hydroxyphenylethyltriazole*, $\text{NPh} \begin{smallmatrix} \text{C}^{\text{Et}}\text{N} \\ \text{N}=\text{C}\cdot\text{OH} \end{smallmatrix}$, is obtained from propionylphenylsemicarbazide under the influence of 10 per cent. potash; it crystallises from alcohol in long, four-sided prisms, and melts at 191—192°.

Isobutyrylphenylsemicarbazide, $\text{CHMe}_2\cdot\text{CO}\cdot\text{NPh}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2$, dissolves with some difficulty in boiling alcohol, and crystallises in short needles which melt at 219°.

3 : 1 : 5-*Hydroxyphenylisopropyltriazole*, $\text{NPh} \begin{smallmatrix} \text{C}^{\text{Pr}^{\beta}}\text{N} \\ \text{N}=\text{C}\cdot\text{OH} \end{smallmatrix}$, crystallises from alcohol in slender needles, and melts at 242°; it dissolves readily in ammonia, crystallising from the liquid in long, four-sided prisms. The *hydrochloride* crystallises in beautiful, lustrous prisms, and the *silver* derivative forms small, transparent crystals; the *acetyl* derivative crystallises in rhombic plates, and melts at 93°.

Butyrylphenylsemicarbazide, $\text{CH}_2\text{Et}\cdot\text{CO}\cdot\text{NPh}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2$, crystallises in white needles and melts at 184°. 3 : 1 : 5-*Hydroxyphenylpropyltriazole* is obtained from it, and crystallises in rhombic plates which melt at 160°.

Isovalerylphenylsemicarbazide, $\text{CH}_2\text{Pr}^{\beta}\cdot\text{CO}\cdot\text{NPh}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2$, crystallises in needles, and melts at 209—210°. It gives rise to 3 : 1 : 5-*hydroxyphenylisobutyltriazole*, which crystallises from alcohol in well-defined rhombohedra, and melts at 164—165°; the *benzoyl* derivative crystallises in four-sided prisms, and melts at 87—88°.

α -*Benzoylphenylsemicarbazide*, $\text{NPhBz}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2$, crystallises from alcohol, and melts at 210—211°. 3 : 1 : 5-*Hydroxydiphenyltriazole* is obtained from it, and crystallises in long needles, melting at 290°; the *acetyl* derivative crystallises in four-sided plates or flat needles, and melts at 130—131°.

Cinnamoylphenylsemicarbazide, $\text{CHPh}\cdot\text{CH}\cdot\text{CO}\cdot\text{NPh}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2$, is sparingly soluble in the ordinary media, and crystallises in needles melting at 241—242°. 3 : 1 : 5-*Hydroxyphenylstyryltriazole* crystallises from boiling glacial acetic acid in needles, and melts at 287°; potassium permanganate oxidises it to 3 : 1-hydroxyphenyltriazole (*loc. cit.*), which melts at 273—274°. The *sodium* derivative contains $3\frac{1}{2}\text{H}_2\text{O}$, and exhibits feeble, yellowish-green fluorescence.

M. O. F.

Synthesis of Diphenyltetrazole. By EDGAR WEDEKIND (*Ber.*, 1896, 29, 1846—1855). The possible occurrence of tautomerism amongst substituted tetrazole derivatives has led the author to synthesise diphenyltetrazole on the lines developed by von Pechmann and Wedekind (*Abstr.*, 1895, i, 574); no indication of the existence of isomeric forms has been observed, and the substance is even more stable than tetrazole.

Formazylparamethoxybenzene, $\text{NHPh}\cdot\text{N}\cdot\text{CPh}\cdot\text{N}\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{OMe}$, is obtained by cautiously adding alcoholic benzaldehyde and phenylhydrazine, mixed with diazotised para-anisidine, to alcoholic potash, the liquid being vigorously agitated during the operation, which is carried on at 25—35°. On adding alcohol to the solution in chloroform, it separates in green prisms having metallic lustre; it melts at 154°.

and develops a magnificent violet coloration with fuming hydrochloric acid.

Paramethoxytriphenyltetrazolium chloride, $\text{CPh} \begin{smallmatrix} \text{N} \cdot \text{NPh} \\ \text{N} \cdot \text{NCl} \cdot \text{C}_6\text{H}_4 \cdot \text{OMe} \end{smallmatrix}$, is produced on treating the foregoing compound with amylic nitrite and alcoholic hydrochloric acid. The action of aqueous potassium iodide converts it into the tetrazolium iodide, crystallising from water or dilute alcohol in prisms, which melt indefinitely at 135—140°.

Parahydroxytriphenyltetrazolium chloride, $\text{CPh} \begin{smallmatrix} \text{N} \cdot \text{NPh} \\ \text{N} \cdot \text{NCl} \cdot \text{C}_6\text{H}_4 \cdot \text{OH} \end{smallmatrix}$, is obtained on heating the methoxy-derivative with concentrated hydrochloric acid for four hours at 150—160°; it crystallises from water in lustrous, yellowish needles, and melts at 243—244°, becoming black. The substance has some of the properties of phenol, bromine water producing a yellow precipitate in dilute solutions, whilst concentrated nitric acid gives rise to a substance resembling picric acid, crystallising in needles which melt at 110—112°. The solutions in alkalis are orange-red, and the sparing solubility of the nitrate is very characteristic, the precipitate in dilute solutions resembling silver chloride. Subcutaneous injection causes paralysis of the extremities in rabbits and frogs, ultimately inducing death when administered in doses of 0.16 gram per kilogram weight; the substance, however, appears to undergo no change in the system.

Diphenyltetrazole, $\text{CPh} \begin{smallmatrix} \text{N} \cdot \text{NPh} \\ \text{N} \cdot \text{N} \end{smallmatrix}$, is formed on oxidising parahydroxytriphenyltetrazolium nitrate with potassium permanganate; it crystallises from alcohol in colourless, lustrous needles, and melts at 106—107°. It is insoluble in water, but dissolves readily in organic solvents, excepting cold alcohol; it is indifferent towards concentrated nitric acid, but on adding potassium nitrate to the solution in concentrated sulphuric acid at 100°, a white substance is produced which melts at 170°.

Formazylparahydroxybenzene, $\text{NPh} \cdot \text{N} \cdot \text{CPh} \cdot \text{N} \cdot \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{OH}$, is obtained on reducing parahydroxytriphenyltetrazolium chloride with ammonium sulphide; it sinters at 110°, and melts at 153—155°. The solution in concentrated sulphuric acid is green. M. O. F.

An Azonium Chloride isomeric with Diphenylfluorindine Dihydrochloride. By FRIEDRICH KEHRMANN and H. BÜRGIN (*Ber.*, 1896, 29, 1820—1822).—The hydrochloride, $\text{C}_{30}\text{H}_{22}\text{N}_4\text{Cl}_2$, is obtained on heating the hydrochloride of the red oxidation product of orthoamidodiphenylamine and the hydrochloride of the base with benzoic acid at 260°, and, after dissolving the product in sufficient boiling alcohol to retain the benzoic acid in solution when the liquid cools, treating it with hydrochloric acid. It crystallises in green needles with metallic lustre, and the solution in water is blue. The substance is isomeric with the dihydrochloride of diphenylfluorindine (this vol., i, 512), which is produced along with it in small quantity. M. O. F.

Stereoisomeric Coniines. By RICHARD WOLFFENSTEIN (*Ber.*, 1896, 29, 1956—1959).— γ -Coniceine, which is obtained along with

coniine from *Conium maculatum*, yields the latter base on reduction with sodium and ethylic alcohol; the modification, however, is optically inactive, and thus a convenient means is afforded of obtaining *i*-coniine.

Ladenburg's isoconiine was stated to form a dimorphous platinum-chloride, the modifications melting at 175° and 160° respectively (Abstr., 1893, i, 442); the author (Abstr., 1894, i, 627) has shown that the former salt is *d*-coniine platinumchloride, and the present communication establishes the identity of the form which melts at 160° with the platinumchloride of *i*-coniine. This salt forms bright red, monoclinic crystals, and the axial angle is $64^{\circ} 30'$ (compare Abstr., 1894, i, 307); a parallel crystallographic examination of the platinumchlorides from both sources has placed their identity beyond question.

Isoconiine, therefore, is a mixture of dextrorotatory coniine with the inactive modification. M. O. F.

Glutineptones. By CARL PAAL (Ber., 1896, 29, 1536; compare the vol., i, 455; Ber., 29, 1084).—It was previously stated that the deamidonitrosopeptone was easily soluble in methylic alcohol and water, but only slightly soluble in hot absolute methylic alcohol. The latter statement refers to deamidonitrosopeptone which is almost insoluble in methylic alcohol. J. F. T.

Deamidoalbumin. By HUGO SCHIFF (Ber., 1896, 29, 1354—1356).—In addition to the diamides previously mentioned (this vol., i, 284), tartronamide, dimethylmalonamide, and ethyloxamide give the biuret reaction. Egg albumin, which acts in a similar manner, is converted by the action of sodium nitrite and dilute acetic acid into *deamidoalbumin*, which is a straw-coloured, insoluble compound, containing 14.7 per cent. of nitrogen; that is, about 1 per cent. less than albumin. It does not contain oxides of nitrogen, does not give the biuret reaction, and reacts only slightly, if at all, with Millon's reagent. It is more slowly digested than albumin, and the resulting *deamidopeptone* gives a yellow coloration with copper sulphate and potash, but not the biuret reaction. When albumin is heated with potash (5–6 per cent.) until about 2 per cent. (? of nitrogen) has been evolved as ammonia, the residue gives the biuret reaction only feebly. This deamidopeptone differs from that described by Paal (this vol., i, 455). The author believes that albumin contains both non-basic amido-groups such as $\text{CO}\cdot\text{NH}_2$ and $\text{CS}\cdot\text{NH}_2$, and basic ones (amido-acids), the appearance of the biuret reaction is conditioned by the presence of the former, which, whilst comparatively unstable towards alkali, are almost unaffected by acids, and therefore remain intact in the preparation of Paal's deamidopeptone. J. B. T.

Organic Chemistry.

Formation of Gaseous and Liquid Hydrocarbons by the Action of Water on Carbides. By HENRI MOISSAN (*Compt. rend.*, 1896, **122**, 1462—1467).—Metallic carbides may be divided into two groups, those which are decomposed by water, like the carbides of the alkali and alkaline earth metals, aluminium, and the cerium metals, and those which are not decomposed by water, such as molybdenum, tungsten, and chromium carbides.

The production of gaseous hydrocarbons in all cases in which the carbides are decomposed by water, and the formation of considerable quantities of liquid, and even solid hydrocarbons in some cases (from uranium carbide, for instance), lead to the supposition that similar decompositions may play an important part in the production of natural hydrocarbons, the metallic carbides having been formed in the interior of the earth. It is possible also that certain volcanic phenomena, and especially those eruptions or stages of eruptions in which gaseous and liquid hydrocarbons are evolved, may be due to the sudden contact of water with large masses of metallic carbides.

C. H. B.

Preparation of Chloroform from Carbon Tetrachloride. [ANONYMOUS] (*Chem. Centr.*, 1896, i, 362—363; from *L'Union Pharm.*, 1895, 11).—The manufacture of chloroform from carbon tetrachloride can be carried out by heating the latter with zinc and dilute sulphuric acid in an apparatus similar to that used for the manufacture of aniline. The hydrogen chloride which is produced may either be collected and condensed or utilised in the reaction itself; in the latter case, the carbon tetrachloride is treated with zinc and hydrochloric acid in an autoclave without heating.

A. H.

Acetylene as an Illuminating Agent. By G. TROUVÉ (*Compt. rend.*, 1896, **122**, 1338—1342).—The author describes portable lamps similar in outward appearance to paraffin lamps, in which acetylene is generated by the action of water on calcium carbide. Provision is made for drying the gas, and the burner is at some height above the generator. Where a large supply of the gas is needed, the generators may be attached to a gas holder of the ordinary form. Two such holders are used, the gas in one being cooled and dried whilst the other is being either emptied or filled, as the case may be. The author attaches considerable importance to the proper cooling and drying of the gas before it is burnt.

C. H. B.

Double Cyanides. By RAOUL VARET (*Compt. rend.*, 1896, **123**, 118—119).—The author has extended his researches on the double cyanides (this vol., ii, 513) to those of silver cyanide and nickel cyanide with the cyanides of the alkalis and alkaline earths. For the same group of salts, for example, the compounds of silver cyanide

with potassium, sodium, barium, calcium and strontium cyanides, the different members have practically the same heat of formation in a state of solution. Further, none of the compounds can be decomposed by dialysis.

These double cyanides are regarded as salts of complex acids which do not exist in the free state, or else are extremely unstable like hydroargenticocyanic acid. J. J. S.

The Colour of the Alcohols compared with that of Water. By WALTHÉRE SPRING (*Zeit. anorg. Chem.*, 1896, **12**, 253—260).—The author has compared the colour of the first members of the series $C_nH_{2n+1}OH$ with that of water. Methylic alcohol is greenish-blue, ethylic alcohol is similar in colour but less intense, and amylic alcohol is greenish-yellow. The pure blue colour of water is gradually more and more mixed with green as one ascends the homologous series. A column of water 26 metres long corresponds in colour with a column 0.314 metre long of a standard 16.32 per cent. copper chloride solution, whilst the colour of a column of methylic or ethylic alcohol corresponds in colour to a column of the copper solution 0.012 or 0.006 metre long respectively. The difference in colour is due to the presence of the carbon chain, and this is clearly seen by comparing the spectra of the compounds. The hydroxyl group absorbs the red rays, and the carbon chain the violet and blue rays, in accordance with the number of the carbon atoms. This is clearly shown in the case of light petroleum, a mixture of the hydrocarbons C_6H_{14} to C_8H_{18} ; the colour is yellow without the slightest tinge of green, and its spectrum shows only green, orange, and red.

A comparison of the transparency of the compounds gave water = 1, methylic alcohol = 0.98629, ethylic alcohol = 0.98383, amylic alcohol = 0.96576, petroleum = 0.96568. E. C. R.

Action of Chlorine on Glycerol in Presence of Iodine. By AL. J. ZAHARIA (*Chem. Centr.*, 1896, i, 100; from *Bull. Soc. Sci. Fisice*, **4**, 133—136).—When chlorine is passed through glycerol containing iodine, an oil distils over which contains hexachloracetone, boiling at 199—201°. The residue contains trichlorolactic acid, which melts at 124° and boils at 140—170° (pressure = 45 mm.), together with mono- and di-chlorhydrin, oxalic and formic acids, and a substance which reduces Fehling's solution and gives with phenylhydrazine a compound melting at 255°. A. H.

Tetrallylammonium. By N. A. ORLOFF (*Chem. Centr.*, 1896, i, 199; from *Pharm. Zeit. Russ.*, **34**, 755—758).—The aluminium alum of tetrallylammonium loses its water of crystallisation when heated, and then forms a brittle mass which is soluble in water. The aqueous solution gives a red precipitate with a solution of bismuth in potassium iodide. Baryta water produces tetrallylammonium hydroxide, which, like the tetramethyl compound, forms soluble salts with uric acid. The author proposes to use the compound as a solvent for uric acid. The chromium alum of tetrallylammonium

has much the same properties as the corresponding aluminium alum. The iron alum could not be obtained.

A note is added to the effect that a good yield of methylic or ethylic iodide can be obtained by the action of potassium iodide and hydrochloric acid on the corresponding alcohol. If sulphuric acid be used, a little granulated zinc should be added. A. H.

Biuret Compounds. By HUGO SCHIFF (*L'Orosi*, 1896, 19, 109—115).—A good yield of biuret is easily obtained by converting carbamide into its hydrochloride with dry hydrogen chloride, heating the product gradually to 130° , aspirating away hydrogen chloride, and extracting ammonium chloride and unaltered carbamide with water; on boiling the residue with 6 per cent. alcoholic potash, all the biuret dissolves, and is partially deposited as *biuret potassium hydroxide*, $C_2H_5N_3O_2.KHO$, on cooling; this crystallises in long needles, is sparingly soluble in hot alcoholic potash, and is decomposed at 90° by water or by the atmospheric carbonic anhydride. The corresponding *sodium* compound, $C_2H_5N_3O_2.NaHO$, is very similar.

On adding mercuric nitrate to a hot aqueous solution of biuret, a white, crystalline *salt* of the composition $C_2H_5N_3O_2.HgO$, is deposited; the mother liquor, on partial neutralisation with potash or potassium carbonate, deposits a caseous, yellow, flocculent *substance* of the composition $Hg(C_2H_5N_3O_2)_2.2HgO$.

Similarly, green, crystalline, copper *compounds*, consisting of $2C_2H_5N_3O_2$ with $CuSO_4$, $Cu(NO_3)_2$, or $CuCl_2$, separate on mixing aqueous or alcoholic solutions of the constituents; these double compounds are dissociated by much water.

On adding concentrated copper acetate solution to biuret potassium hydroxide, and then precipitating with alcoholic potash, a red caseous mass, soon changing into deep red laminae or long, crimson needles, is deposited; the formation of this substance constitutes the well-known test for biuret. It is very soluble in water, and readily alters in the air; from a study of its formation and decomposition, the author concludes that it has the composition



The compounds of biuret with nickel salts are analogous to those with copper salts; *compounds* in which $2C_2H_5N_3O_2$ is combined with $NiSO_4$ or $NiCl_2$ have been prepared and analysed.

In order that a diamide shall give the biuret reaction with metallic salts, it seems necessary that it should contain at least two of the groups $-CO.NH_2$ combined with each other, or with a single atom of carbon or nitrogen, or with one or more groups $-CO.NH-$ existing in an open chain. Thus, the biuret reaction is given by oxamide, hydroxyoxamide, thiobiuret, malonic diamide, tartronic diamide, oxaluramide, oxalyldicarbamide, isosuccinic diamide, dimethylmalonic diamide, and phenyloxamide, but not by oxalyldiureide, carbonyldicarbamide, or succinic diamide. W. J. P.

Reduction of Nitrates and Formation of Quaternary Nitrogenous Compounds in Plants. By A. BACH (*Compt. rend.*, 1896, 222)

122, 1499—1502).—When formaldehyde is oxidised by nitric acid at 80° , carbonic anhydride, nitrous oxide, nitric oxide, nitrogen, and methylic nitrite are given off, and the liquid contains formaldehyde, methylic alcohol, polymerised trioxymethylene, and ammonium nitrate, with small quantities of methylamine nitrate. Trioxymethylene yields the same products with the exception of methylic nitrite and methylic alcohol. If formaldoxime is formed, it is immediately destroyed. If, however, 5 grams of trioxymethylene is suspended in 100 c.c. of ether, and treated for many hours at 20° with a slow current of nitrogen oxides from sodium nitrite and sulphuric acid, formaldoxime and trioximidomethylene are formed, and give all the reactions described by Scholl (Abstr., 1891, 663). Formamide cannot be isolated from the product of this reaction, but its characteristic mercury compound is formed when formaldehyde is oxidised by nitric acid in presence of mercuric chloride.

Formaldoxime is the first quaternary term of the reduction of nitric acid by formaldehyde, and this fact lends support to the hypothesis that the formation of nitrogen compounds in plants is brought about by the reduction of the nitrates by formaldehyde and the other aldehydic and ketonic derivatives present in the plants.

C. H. B.

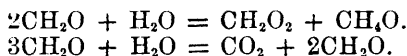
Aliphatic Thiocarbimides. By GIACOMO PONZIO (*Gazzetta*, 1896, **26**, i, 323—327; compare Abstr., 1895, i, 324).—The author has investigated the fact observed by Hofmann, that in preparing a thiocarbimide by distilling a solution of an alkyl dithiocarbamate with mercuric chloride in a current of steam, twice the theoretical quantity of mercuric chloride has to be used in order to obtain a good yield. The cases investigated were those of the thiocarbamates obtained by the action of carbon bisulphide on propylamine, isobutylamine, isoamylamine, heptylamine, and isoundecylamine. If the theoretical proportion of mercuric chloride be used, hydrogen sulphide is evolved, and never more than a 40 per cent. yield of thiocarbimide is obtained, whilst variable and considerable proportions of the corresponding dialkylthiocarbamide are produced; if, however, twice as much mercuric chloride is used, and the evolution of hydrogen sulphide thus avoided, more than a 90 per cent. yield of thiocarbimide, and no thiocarbamide, are obtained. When the smaller proportion of mercuric chloride is used, it is only natural to conclude that the liberated hydrogen sulphide acts on the alkylthiocarbimide, converting it into the corresponding carbamide and carbon bisulphide. The prevalent opinion that hydrogen sulphide is without action on the aliphatic thiocarbimides is erroneous, for the author finds that, on passing hydrogen sulphide into ethyl-, isobutyl-, and heptylthiocarbimides suspended in water, they are wholly converted into the corresponding thiocarbamides.

Heptylthiocarbimide, $C_7H_{15}N:CS$, obtained by the general method from heptylamine, is a colourless, very mobile liquid, which is lighter than water, and has a slightly unpleasant odour; it boils at 238° under 732.9 mm. pressure.

Diheptylthiocarbamide, $(C_7H_{15}NH)_2CS$, may be prepared by the action of alcohol on heptylammonium heptyldithiocarbamate, or by

passing hydrogen sulphide through boiling water containing heptylthiocarbimide in suspension; it is sparingly soluble in water, light petroleum, or alcohol, and crystallises in lustrous scales melting at 58—59°. W. J. P.

Action of Water on Formaldehyde. By MARCEL DELÉPINE (*Compt. rend.*, 1896, **123**, 120—122).—Paraformaldehyde, when heated with its own weight of water in sealed tubes at 200°, yields formic acid, methylic alcohol, and carbonic anhydride. These are probably formed according to the equations

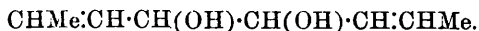


A small quantity of carbon monoxide is usually formed by the decomposition of a portion of the formic acid.

If a similar decomposition can be brought about at ordinary temperatures in vegetable tissues, then the author thinks that it would readily account for the presence of free formic acid, and of methylic alcohol in many plants. It also accounts for the fact to which Schloesing (*Compt. rend.*, 1885, **100**, 1237) has drawn attention, namely, the excess of hydrogen over oxygen—as required for a carbohydrate—which exists in most plants. J. J. S.

Reduction of Crotonaldehyde. By ER. CHARON (*Compt. rend.*, 1896, **123**, 123—125; compare Lieben and Zeisel, *Monatsh.*, **1**, 823).—On reducing a 10 per cent. solution of crotonaldehyde with a copper-zinc couple in the presence of acetic acid, the author has obtained a mixture of normal butaldehyde, crotonylic alcohol, and the pinacone of crotonaldehyde. The liquid containing the products of reduction is extracted four times with ether, and the ether is carefully evaporated, a Le Bel column being used. The residue is distilled under 20—30 mm. pressure, and the portion which passes over below 115° is freed from acetic acid, and then carefully fractionated at the ordinary pressure; normal butaldehyde (b. p. 75°) first passes over, and finally, between 110° and 122°, the impure *crotonylic alcohol*. The latter is best purified by distillation over quicklime, although this entails a considerable loss of material. As thus obtained, the alcohol is a colourless liquid with a slightly pungent odour; it boils at 122—123°, has a sp. gr. = 0.8726 at 0°, and readily combines with bromine.

The residue, left on distilling off the two above-mentioned products under a pressure of 20—30 mm., is further fractionated under a pressure of 9 mm., when it yields a considerable quantity of a liquid boiling at 120—122°; this is the *pinacone of crotonaldehyde*,



It readily darkens on exposure to the air, and has a sp. gr. = 0.9833 at 0°. It readily unites with bromine, and yields also a diacetyl derivative. J. J. S.

Synthesis of Methylheptenone. By PHILIPPE BARBIER and LOUIS BOUVEAULT (*Compt. rend.*, 1896, **122**, 1422—1424).—When the

amylenic bromide, $\text{CMe}_2\text{Br}\cdot\text{CH}_2\cdot\text{CH}_2\text{Br}$, is boiled with two molecular proportions of sodioacetylacetone in presence of ether, it yields the compound $\text{CMe}_2\cdot\text{CH}\cdot\text{CH}_2\cdot\text{CH}(\text{COMe})_2$ as a colourless, oily liquid; this boils at $112\text{--}115^\circ$ under a pressure of 10 mm. and when treated with concentrated sodium hydroxide solution, splits up into sodium acetate and methylheptenone, $\text{CMe}_2\cdot\text{CH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{COMe}$.

The methylheptenone thus obtained is identical in all its properties with the natural product from lemon-grass oil and from linaloes, and forms the same semicarbazone melting at $133\cdot5\text{--}134^\circ$. Since methylheptenone is readily converted into geranic acid (this vol., i, 445), it follows that a complete synthesis of the latter can be made.

In the decomposition of the isoamylacetylacetone by sodium hydroxide, the yield of methylheptenone is small, and the chief product is a ketone, $\text{C}_{10}\text{H}_{14}\text{O}$, which boils at $215\text{--}225^\circ$.

C. H. B.

Action of Ethylic Sodacetoacetate on Ethylic β -Bromo-levulinate. By WILLIAM O. EMERY (*J. pr. Chem.*, 1896, [2], 53, 557—560; compare this vol., i, 414, and Knorr, *Abstr.*, 1886, 331).—By repeating Knorr's experiments (*loc. cit.*), the author has obtained a liquid and a solid ethereal salt; the latter, when purified, crystallises in white needles, melts at 92° , and is soluble in the usual solvents, but not in cold water. Analysis of the salt leads to the formula $\text{C}_{13}\text{H}_{20}\text{O}_6$, but it remains undecided whether



or $\text{COMe}\cdot\text{CH}_2\cdot\text{CH}(\text{COOEt})\cdot\text{CH}(\text{COMe})\cdot\text{COOEt}$ represents the constitution of the compound. When heated with strong hydrochloric acid, the ethereal salt is hydrolysed, and carbonic anhydride is at the same time eliminated, the product being a monobasic acid, $\text{C}_8\text{H}_{10}\text{O}_3$, which melts at 93° . Alcoholic ammonia at 100° converts the ethereal salt into an amide, $\text{C}_{11}\text{H}_{17}\text{NO}_5$.

A. G. B.

Isanic acid. By ALEXANDRE HÉBERT (*Compt. rend.*, 1896, 122, 1550—1553).—The seeds from I'Sano in Loango, known to the natives as *ungueko*, are derived, according to H. Lecomte, from a large tree belonging to the olacineæ. These seeds contain fatty matter which is extracted by benzene and forms a reddish, viscous, rapidly drying oil, which contains 86 per cent. of liquid fatty acids, the lead salts of which are completely soluble in ether. The fatty acids can be separated by fractionally precipitating the mixed ammoniacal salts with barium chloride. They consist of a mixture of 15 per cent. of oleic acid, 75 per cent. of linoleic acid, and 10 per cent. of a new solid acid, which the author calls *isanic acid*. It forms large, flaky crystals, soluble in most organic solvents, and in solutions of alkalis. It has a peculiar odour, is optically inactive, is not volatile in steam, but can be distilled with partial decomposition in a vacuum. When exposed to the air, the acid alters rapidly and absorbs oxygen, with formation of a rose coloured compound which is insoluble in ether, and is very stable. The salts exhibit similar instability. Cryometric determinations show that the acid has a molecular weight of 217,

and it seems to have the composition $C_{14}H_{20}O_2$, and to belong to the $C_nH_{2n-2}O_2$ series. It absorbs 2 mols. of bromine, but yields no definite products when heated at 200° with concentrated hydriodic acid. When exposed to light, or when treated with acid mercuric nitrate, it shows no condensation similar to that which occurs with oleic acid.

Ammonium isanate is soluble in water and crystallises in nacreous plates; the barium salt is microcrystalline and dissolves in alcohol and chloroform; the lead and silver salts are amorphous.

C. H. B.

Succinic and Glutaric acids. By KARL AUWERS (*Annalen*, 1896, **292**, 132—243).—I.—The author has collected the references in the literature to dicarboxylic acids of the formula $C_7H_{12}O_4$, pointing out that among the 24 possible isomerides, all are known with the exception of tertiary butylmalonic acid, asymmetric methyl-ethylsuccinic acid, and the two $\alpha\beta$ -dimethylglutaric acids. Other acids having this formula have been also described, but the second trimethylsuccinic acid and the third symmetrical $\alpha\alpha_1$ -dimethylglutaric acid do not exist (Abstr., 1895, i, 505), whilst metapimelic acid, and syrupy trimethylsuccinic acids are impure substances. With regard to isopimelic acid, first obtained by Bauer and Schuler, and subsequently described by Hell and Schad, the author, although unable to adduce direct evidence, is of opinion that this substance is the missing methylethylsuccinic acid.

II. [With F. SCHLOSSER].—Comparative experiments have been made on the relative volatility of substituted succinic and glutaric acids in an atmosphere of steam, the influence of sulphuric acid being also studied. From the tabulated results, which appear in the paper, the following conclusions are drawn. 1. The addition of sulphuric acid increases the volatility, but its influence differs widely among the various acids. 2. Substitution of methyl groups increases the volatility of succinic and glutaric acids. 3. The position of the substituent influences the property in question. 4. Substituted succinic acids are more volatile, and in general considerably more so, than glutaric acids containing the same number of alkyl groups; so marked is this difference that the author regards the property as of value in distinguishing between substituted succinic and glutaric acids, and in this connection points out that camphoric acid is but slightly volatile.

III. 1. [With F. SCHLOSSER].—Diisopropylsuccinic acid is obtained in the form of the ethylic salt by heating ethylic α -bromisovalerate with finely divided silver (compare Hell and Mayer, *Ber.*, 1889, **22**, 48); it crystallises from hot water, or dilute alcohol, in long, lustrous needles and prisms, and melts at 180° . It is noteworthy that although symmetrical, disubstituted succinic acids usually occur in two modifications, all attempts to convert diisopropylsuccinic acid into an isomeric modification have hitherto been unsuccessful; another remarkable property of this acid is the electrical conductivity, which is $K = 0.3148$, whilst the constants for ethyldimethylsuccinic and propyldimethylsuccinic acids, the highest among the 30 alkylated succinic acids hitherto examined, are 0.0556

and 0.0551 respectively. The anhydride of diisopropylsuccinic acid is a colourless oil which boils at 255—257° under atmospheric pressure, and solidifies in a freezing mixture; it may be heated during several hours with boiling water without undergoing conversion into the acid. The *imide* is obtained by heating the anhydrous ammonium salt in sealed tubes for 6 hours at 230—240°; it crystallises from petroleum in transparent prisms, and melts at 62°. The *anilic acid* crystallises from dilute alcohol in white needles and melts at 179—180°; the *anil* also forms needles, and melts at 95—96°. The *paratolilic acid* and *paratolil* melt at 172—173° and 113—115° respectively, whilst the β -*naphthilic acid* and β -*naphthil* melt at 164° and 126° respectively. Diisopropylsuccinic acid resists the action of bromine.

III. 2. [With TH. SCHIFFER and F. SCHLOSSER].—The *paratolil* of tetramethylsuccinic acid crystallises from dilute alcohol in white needles, melting at 90°; the β -*naphthil*, which also forms needles, melts at 152°. The *benzidine* derivative, $C_{26}H_{22}N_2O_2$, melts at 196°, and the *orthophenylenediamine* derivative crystallises in long, lustrous needles, and melts at 142.5—143°. The *hydrogen methylic salt* crystallises from petroleum in small, white plates, melting at 68°, whilst the *methylic salt* crystallises in prisms, melting at 31°; the *hydrogen ethylic salt* is a viscous oil, which yields ethylic alcohol and tetramethylsuccinic anhydride when heated.

III. 3. [With F. SCHLOSSER].—*Asymmetric methylethylsuccinic acid*, $COOH \cdot CMeEt \cdot CH_2 \cdot COOH$, is obtained in the form of its ethylic salt by the action of ethylic sodiomalonate on ethylic α -bromomethylethylacetate, and distillation of the tricarboxylate, thus produced; it crystallises from benzene in lustrous prisms, and when previously dried, melts at 102—103°, the transparent prisms which separate from water melting at the same temperature, and losing water at 190—200°. The electrical conductivity is $K = 0.0248$. The *nickel salt* is a bright green, hygroscopic powder. The *paratolil* crystallises from petroleum in slender, lustrous needles, and melts at 64—65°.

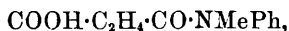
III. 4. [With F. SCHLOSSER].—The electrical conductivity of asymmetric dimethylsuccinic acid is $K = 0.00843$, and it melts at 140—141° (compare Béhal, this vol., i, 179). The *anilic acid* melts at 190—191°, evolving gas (*loc. cit.*) and the *anil* melts at 84—86°; the *paratolilic acid* and *paratolil* melt at 185° and 112—113° respectively, and the β -*naphthilic acid* and β -*naphthil* at 181° and 147—148° respectively.

III. 5. [With J. HARGER].—Compounds analogous to the anils and anilic acids are obtained by the action of secondary bases on succinic anhydride, which also combines with aniline derivatives containing a negative substituent; whilst, however, the anilic acids of the latter class are readily converted into anils under the influence of heat, the corresponding derivatives of secondary bases are resolved into a mixture of succinic acid and tetrasubstituted succinamide.

The *paratolilic acid* melts at 179—180°, and has the same composition as the substance melting at 157° obtained by von Bechi from paratolylsuccinimide under the influence of barium hydroxide; the *paratolil* melts at 151°, and the *paratolylamide* crystallises in nacreous

leaflets, and melts at 207° , although according to von Bechi, the melting point is 148° . The β -*naphthilic acid* melts at 184 – 185° , and the β -*naphthil* at 183° , Pellizzari and Matteucci giving 190 – 192° and 180° , respectively; the β -*naphthylamide* crystallises in nacreous plates, and melts at 219° .

The *orthonitranilic acid* melts at 132 – 132.5° , and the *orthonitranil* at 155.5 – 156° ; the *paranitranilic acid* crystallises in lemon yellow needles, and the *paranitranil* melts at 203 – 204° . The *orthocarboxyanilic acid*, obtained from succinic anhydride and anthranilic acid, melts at 178° , whilst the *orthocarboxyphenylamide* is an amorphous powder, melting at 191° . The *methylamlilic acid*,



melts at 91 – 92.5° , and the *methylanilide*, $\text{C}_2\text{H}_4(\text{CO} \cdot \text{NMePh})_2$, at 154.5 – 155° , whilst the *ethylamlilic acid* and *ethylanilide* melt at 92 – 93° and 101 – 101.5° , respectively. The *diphenylaminic acid*, $\text{COOH} \cdot \text{C}_2\text{H}_4 \cdot \text{CO} \cdot \text{NPh}_2$, melts at 116.5° , and the *tetraphenyldiamide*, $\text{C}_2\text{H}_4(\text{CO} \cdot \text{NPh}_2)_2$, at 231° .

IV. 1.—Whilst the formation of anils and anilic acids renders the identification of substituted succinic acids a simple matter, the production of two isomerides surrounds with difficulty the application of this method to asymmetric glutaric acids; the anils, moreover, arising from the latter source, are either unimolecular, having the structure $\text{CH}_2 < \begin{smallmatrix} \text{CH}_2 \cdot \text{CO} \\ \text{CH}_2 \cdot \text{CO} \end{smallmatrix} > \text{NR}$, or bimolecular, as represented by the

formula $\text{CH}_2 < \begin{smallmatrix} \text{CH}_2 \cdot \text{CO} \cdot \text{NR} \cdot \text{CO} \cdot \text{CH}_2 \\ \text{CH}_2 \cdot \text{CO} \cdot \text{NR} \cdot \text{CO} \cdot \text{CH}_2 \end{smallmatrix} > \text{CH}_2$. The polymeric anils are less readily fusible than the monomolecular compounds, and the anhydrides of dimethylglutaric acid, already described (*Abstr.*, 1895, i, 210), belong, therefore, to the former class; they resist the influence of hydrolytic agents, and by means of this property may be freed from the unimolecular anils, which are readily converted into the anilic acids.

The general method of preparing the unimolecular anhydrides consists in heating the anilic acid with acetic chloride, whilst the polymerides are most conveniently obtained by boiling the anilic acid in a vacuum for a few minutes.

IV. 2. [With W. SINGHOF].—The bimolecular paratolil of $\alpha\alpha_1$ -dimethylglutaric acid has been already described (*loc. cit.*), and melts at 233° ; the *unimolecular paratolil*, obtained by digesting the paratolilic acid with acetic chloride, crystallises from alcohol in prisms and rhombs, both of which melt at 120° .

It has been observed that the anhydride common to the fumaroid and maleinoid forms of $\alpha\alpha_1$ -dimethylglutaric acid, yields the latter modification exclusively on hydrolysis, whilst the action of acids on a dibasic metallic salt liberates the particular form from which it is derived; the cyclic *methylenic* and *ethylenic* salts of fumaroid $\alpha\alpha_1$ -dimethylglutaric acid have been therefore prepared. The former salt is rapidly hydrolysed by alcoholic potash, yielding the fumaroid modification of the acid.

The author has again established the identity of dimethyldi-

hydroxyglutaric acid, obtained by Zelinsky (Abstr., 1892, i, 437), with the product of the action of caustic soda on dibromodimethylglutaric anhydride (Auwers and Jackson, Abstr., 1890, 1098); it crystallises in the triclinic system.

IV. 3. [With W. SINGHOF].—By heating diethyldicarboxyglutaric acid, and also on treating the ethylic salt with sulphuric acid, Dressel obtained a mixture of acids which melted at 63° , and became clear at 100° ; this has now been resolved into two isomeric α_1 -diethylglutaric acids. The less readily fusible form crystallises from water in small prisms, and melts at 118 – 119° , whilst the electrical conductivity is $K = 0.0055$; the isomeride crystallises from petroleum, melts at 76 – 78° , and has the electrical conductivity $K = 0.00595$. The anhydride is an oil which boils at 282 – 284° , but it is questionable whether this is a homogeneous compound. The anilic acid crystallises in silvery needles, and melts at 133 – 134° , whilst the paratolilic acid melts at 179 – 180° ; the unimolecular paratolil crystallises from petroleum in prisms melting at 76 – 82° , and the bimolecular paratolil melts at 176 – 178° .

IV. 4. [With A. W. TITHERLEY].—Ethylic α -methylcarboxyglutarate, $\text{CMe}(\text{COOEt})_2\text{CH}_2\text{CH}_2\text{COOEt}$, is obtained by the action of ethylic sodiomethylmalonate on ethylic β -iodopropionate; it is a colourless, viscous oil, of sp. gr. = 1.074 at 10.5° , and boils at 164.5 – 165° under a pressure of 15 mm. When treated with equal volumes of boiling water and concentrated sulphuric acid, evaporated on the water bath, and distilled under diminished pressure, it yields α -methylglutaric acid, which crystallises in prisms, and melts at 77 – 78° , as already observed. The anhydride is a colourless oil, which boils at 272 – 275° under atmospheric pressure; when heated with aniline in benzene solution, it yields a mixture, from which the anilic acid has been isolated; this melts at 114 – 115° , whilst another modification melts indefinitely at about 100° . The bimolecular anil crystallises in slender needles and melts at 175 – 176° , and the bimolecular paratolil and bimolecular β -naphthil melt at 170° and 166 – 169° , respectively; two paratolilic acids, melting at 98 – 99° and 126° , respectively, have been prepared, and the β -naphthilic acid melts at 115 – 119° .

IV. 5. [With A. W. TITHERLEY].—Ethylic α -ethylcarboxyglutarate, $\text{CEt}(\text{COOEt})_2\text{CH}_2\text{CH}_2\text{COOEt}$, is prepared from ethylic sodioethylmalonate and ethylic β -iodopropionate; it is a colourless, viscous oil, of sp. gr. = 1.059 at 18° , and boils at 180° and 192° under pressures of 25 mm. and 35 mm., respectively. α -Ethylglutaric acid,



is obtained from the foregoing salt by elimination of ethylic alcohol and carbonic anhydride, followed by hydrolysis; it separates from petroleum in large crystals, melts at 60.5° , and boils at 194 – 196° under a pressure of 30 mm. The electrical conductivity is $K = 0.005852$. The anhydride is a colourless oil, which boils at 275° , and the anilic acid and anil melt at 154.5° and 167 – 168° , respectively. The paratolilic acid, which melts at 145.5° , crystallises from dilute alcohol in lustrous leaflets, and the isomeride melts at 119 – 120° . The paratolil melts at 94 – 95° , and is therefore probably unimole-

cular; the β -naphthilic acids melt at $129\cdot5^\circ$ and 142 — 143° , respectively, and the β -naphthil melts at $127\cdot5^\circ$.

IV. 6. [With A. W. TITHERLEY].—Ethylic α -isopropylcarboxyglutarate, $\text{CPr}^\beta(\text{COOEt})_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{COOEt}$, is obtained by the action of ethylic sodioisopropylmalonate on ethylic β -iodopropionate, the change proceeding less smoothly than the production of the lower homologues; it is a viscous, colourless oil, of sp. gr. = $1\cdot0567$ at 20° , and boils at 197° under a pressure of 33 mm. The diethylic salt, $\text{CPr}^\beta(\text{COOEt})_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{COOH}$, is obtained by heating the triethylic salt with hydrochloric acid during 18 hours; it crystallises from acetic acid in plates, melts at 68 — 69° , and distils at about 300° without undergoing decomposition.

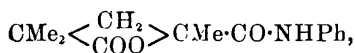
IV. 7. [With E. ZIEGLER].—In order to establish the identity of $\alpha\alpha\alpha_1$ -trimethylglutaric acid and the non-volatile acid melting at 97° and produced by the action of finely divided silver on ethylic α -bromoisobutyrate (compare Hell, this vol., i, 10), the nitrile obtained from mesitonic, or $\alpha\alpha$ -dimethyllevulinic acid, under the influence of hydrogen cyanide, has been submitted to hydrolysis; a lactone is produced, and is converted by hydriodic acid and phosphorus into an acid, which, from its mode of preparation, has the constitution



and is therefore $\alpha\alpha\alpha_1$ -trimethylglutaric acid. This acid is in every respect identical with the substance obtained from ethylic α -bromoisobutyrate; the bromanhydride melts at 114° , and the lactonic acid obtained from it at 103 — 104° . The anilic acid crystallises in white needles, and melts at 165° . $\alpha\beta\beta$ -Trimethylglutaric acid has been recently obtained by Balbiano (Abstr., 1895, i, 552) and Tiemann (*loc. cit.*, 679).

V. [With TH. SCHIFFER and W. SINGHOF].—The behaviour of bromocamphoric anhydride towards bases (Abstr., 1893, i, 525) is regarded by the author as evidence in favour of a glutaric formula for camphoric acid, and the action of bases on the anhydrides of bromo- $\alpha\alpha\alpha_1$ -trimethylglutaric and symmetrical dibromodimethylglutaric acids has been therefore studied, in order to compare them in this respect with bromocamphoric anhydride; the resemblance between the compounds in question is complete, whilst the anhydrides of isodibromosuccinic and citradibromopyrotartaric acids combine with only one molecular proportion of aniline, forming dibromanilic acids, from which hydrogen bromide is not eliminated spontaneously.

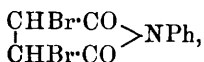
The anilide of hydroxytrimethylglutaric lactone,



is obtained by adding aniline (2 mols.) to the brominated anhydride of $\alpha\alpha\alpha_1$ -trimethylglutaric acid, aniline hydrobromide being formed; the anilide crystallises from very dilute alcohol in small, white needles, and melts at 97° . The amide, produced when ammonia is employed instead of aniline, melts at 134 — 135° ; its constitution is established by hydrolysis, which converts it into the lactone of hydroxytrimethylglutaric acid. The anilide of bromohydroxydi-

methylglutaric lactone, $\text{CMeBr} < \begin{smallmatrix} \text{CH}_2 \\ \text{COO} \end{smallmatrix} > \text{CMe} \cdot \text{CO} \cdot \text{NHPh}$, is obtained by the action of aniline on dibromodimethylglutaric anhydride, and crystallises in lustrous prisms which melt at $137-138^\circ$; the *paratoluidide* melts at 172° , and the *β -naphthalide* at 186° .

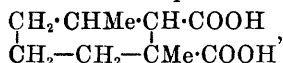
Dibromosuccinanilic acid, $\text{COOH} \cdot \text{CHBr} \cdot \text{CHBr} \cdot \text{CO} \cdot \text{NHPh}$, is produced on adding aniline to a solution of isodibromosuccinic anhydride (Abstr., 1895, i, 20) in benzene; it crystallises in silky needles, and melts, decomposing, at $144-145^\circ$. *Dibromosuccinanil*,



is obtained by heating the anilic acid with acetic chloride; it crystallises in lustrous needles, and melts at 177° . *Bromomaleinanil*, $\begin{array}{c} \text{CH} \cdot \text{CO} \\ || \\ \text{CBr} \cdot \text{CO} \end{array} > \text{NPh}$, is formed when dibromosuccinanilic acid is heated at its melting point; it crystallises in silky needles, and melts at $159-160^\circ$, whilst a compound which is formed along with it, crystallises in golden leaflets melting at 200° . *Dibromosuccinoparatolilic acid* melts at 153° , and spontaneously yields *bromomaleinoparatolil*, which crystallises in lustrous, yellowish needles, and melts at 144.5° ; *dibromosuccino- β -naphthilic acid* is even less stable than the *paratolilic acid*.

Citradibromopyrotartaranilic acid is obtained from aniline and citradibromopyrotartaric anhydride (this vol., i, 131); it crystallises in long, silky needles, and melts at 146° . The *paratolilic acid* also forms needles, and melts at 152° .

VI. [With TH. SCHIFFER.]—A compound having the constitution expressed by Collie's formula for camphoric acid,



should arise from the ethylic salt obtained from ethylic α -bromo-methylpropylacetate and ethylic sodioacetoacetate, by intramolecular condensation, followed by hydrolysis and subsequent reduction. A preliminary experiment has been therefore made with ethylic α -bromisobutylacetate, which yields ethylic α -acetyl- α_1 -isobutylsuccinate by the action of ethylic sodioacetoacetate; the compound obtained by the action of concentrated sulphuric acid on this substance, however, although having the composition $\text{C}_{10}\text{H}_{14}\text{O}_4$, does not exhibit the properties of an unsaturated dibasic acid, and the attempt to synthesise camphoric acid in the manner indicated has therefore been abandoned.

Ethylic α -bromisobutylacetate, $\text{CHMe}_2 \cdot \text{CH}_2 \cdot \text{CHBr} \cdot \text{COOEt}$, is an oil of agreeable, fruity odour, and boils at 101° under a pressure of 24 mm.; at $202-204^\circ$, it distils under atmospheric pressure, a small quantity of hydrogen bromide being eliminated.

Ethylic α -acetyl- α_1 -isobutylsuccinate,



is a heavy oil, which boils at $161-163^\circ$ under a pressure of 20 mm.

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Under the influence of concentrated sulphuric acid, it yields the compound, $C_{10}H_{14}O_4$, which crystallises in small, lustrous needles, and melts at $178-179^\circ$; the *phenylhydrazine derivative*, which is not a simple hydrazone or hydrazide, crystallises from alcohol in small, lustrous needles, and melts at 172° . Alkalis convert the compound $C_{10}H_{14}O_2$ into an *isomeric*, a monobasic acid, which crystallises from benzene, and melts at $141-142^\circ$; when alcoholic ammonia is employed, this substance is also obtained, together with a nitrogenous compound, melting at $105-106^\circ$.
M. O. F.

M. O. F.

Action of Formaldehyde and Hydrochloric acid on Tartaric acid. By W. HENNEBERG and BERNHARD TOLLENS (*Annalen*, 1896, **292**, 53—55).—*Methylenetartaric acid*, $C_5H_6O_6$, is obtained in small quantity when tartaric acid, formaldehyde, and hydrochloric acid are heated in sealed tubes at 150° ; it crystallises from ether in needles containing $\frac{1}{2}H_2O$, and melts at 138 — 140° . Titration with one-third normal caustic soda indicates that the acid is dibasic.

Crystalline methylene derivatives have not been obtained from mucic acid, *d*-glucose, or isosaccharin. M. O. F.

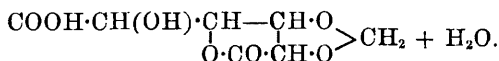
M. O. F.

Dimethylenegluconic acid. By W. HENNEBERG and BERNHARD TOLLENS (*Annalen*, 1896, **292**, 31–39; compare this vol., i, 115).—*Dimethylenegluconic acid*, $C_8H_{12}O_7$, is obtained by heating calcium gluconate with formaldehyde and hydrochloric acid in a reflux apparatus at 110° during an hour; it crystallises in lustrous needles, and melts at 220° . It is somewhat sparingly soluble in water, one part requiring 117.7 parts of the solvent; the specific rotatory power $[\alpha]_D = +41^\circ$. The salts of dimethylenegluconic acid are soluble in water, and the *potassium*, *sodium*, and *ammonium* salts contain $1H_2O$, $1\frac{1}{2}H_2O$, and $2H_2O$ respectively; the *magnesium* salt contains $6H_2O$, and the *calcium* and *strontium* salts $4H_2O$ and $7H_2O$ respectively. The *barium* salt crystallises in octahedra with $4H_2O$; the *copper* salt forms slender, bright blue needles, containing $2H_2O$; whilst the *zinc* and *lead* salts contain $3H_2O$.

Five alternative formulæ are suggested, representing the structure of dimethylenegluconic acid. M. O. F.

M. O. F.

Monomethylenesaccharic acid. By W. HENNEBERG and BERNHARD TOLLENS (*Annalen*, 1896, **292**, 40—53).—*Methylenesaccharic acid*, $C_7H_{10}O_8$, is obtained by heating potassium hydrogen saccharate with formaldehyde and hydrochloric acid, in a reflux apparatus, for 1—2 hours at 110° ; it separates from a dilute solution in beautiful prisms, sometimes a centimetre long. The acid melts at 144 — 146° , losing H_2O at 100° ; in the anhydrous state it melts at 176 — 178° . It dissolves in 41.7 parts of water at 13° , and the specific rotatory power $[\alpha]_D = +117.5^\circ$; its behaviour towards standard alkali is that of a lactic acid, and the authors accordingly express its constitution by the formula,



It resists the action of 5 per cent. sulphuric acid, and concentrated hydrochloric acid, but becomes yellow when heated with alkalis, formaldehyde being eliminated.

The *sodium* salt crystallises from alcohol, with $2\frac{1}{2}\text{H}_2\text{O}$; the *potassium* and *ammonium* salts crystallise in needles containing $1\text{H}_2\text{O}$. The *magnesium* salt contains $1\text{H}_2\text{O}$, and the *calcium* salt, which crystallises in microscopic, six-sided plates, contains $4\text{H}_2\text{O}$; the *strontium* and *barium* salts, $4\text{H}_2\text{O}$; the *copper* salt, $2\text{H}_2\text{O}$, and the *zinc* salt, $3\text{H}_2\text{O}$; whilst the *lead* salt is anhydrous. The *ethylic* salt crystallises in long, slender needles, and melts at $192-194^\circ$, and when treated with hot, one-third normal, caustic soda, neutralises a quantity of the agent which indicates rupture of the lactone ring.

M. O. F.

The Benzene Nucleus. By WILHELM VAUBEL (*J. pr. Chem.*, 1896, [2], 53, 549—557; compare *Abstr.*, 1895, i, 53, 339; this vol., i, 213, 352).—From a review of the behaviour of the dinitrobenzoic acids and of the nitro- and dinitro-phthalic acids with tin and hydrochloric acid, it is concluded that by this treatment (1) an elimination of the carboxyl group does not occur when there is a nitro-group or a second carboxyl group in the meta-position to the carboxyl group; and (2) in the absence of such a protective group an elimination of the carboxyl group will only occur when two negative groups occupy the ortho-positions, or the ortho- and para-positions relatively to the carboxyl group. These observations are discussed in connection with the author's benzene configuration (*Abstr.*, 1894, i, 325).

The bromination of asymmetrical acetometaxylidine yields a bromo-derivative, which melts at $95-96^\circ$, whilst the acetylation of the bromoxylidine (m. p. 45°) obtained by brominating asymmetrical metaxylidine yields a compound which melts at 193° . This fact, which escaped the notice of Wroblewski (*Annalen*, 1878, 192, 215), is here explained by the author's configuration for benzene.

The paper concludes with some remarks on the decomposition of the phenolcarboxylic acids in presence of aromatic bases as elucidated by Cazeneuve (*Chem. Centr.*, 1896, i, 494).

A. G. B.

Action of the Chlorides of Phosphorus on Halogenised Phenols. By AL. J. ZAHARIA (*Chem. Centr.*, 1896, i, 100); from *Bull. Soc. Sci. Fissime*, 4, 130—135).—A mixture of trichlororesorcinol with phosphorus trichloride reacts with phosphorus pentachloride at $250-280^\circ$, with formation of pentachlorobenzene, according to the equation, $\text{C}_6\text{HCl}_3(\text{OPCl}_2)_2 + 2\text{PCl}_5 = \text{C}_6\text{HCl}_5 + 2\text{POCl}_3 + 2\text{PCl}_3$; a certain amount of hexachlorobenzene is also formed. Trichlorophenol, when treated in a similar manner, yields 1:2:4:6-tetrachlorobenzene, melting at $54-55^\circ$, and hydrogen trichlorophenylic phosphate, $(\text{C}_6\text{H}_2\text{Cl}_3\text{O})_2\text{PO}\cdot\text{OH}$, which melts at 230° ; the latter can only be hydrolysed with difficulty, and yields numerous salts. The *methylic* salt melts at $132-133^\circ$.

A. H.

Two Isomerides of Anethoil. By CHARLES MOUREU (*Compt. rend.*, 1896, 123, 57—60).—The author has prepared *orthopropenylanisoil* and the corresponding *meta-compound*, both of which are

isomeric with anethoil (parapropenylanisoil). They were obtained by heating a mixture of propionic anhydride and dry sodium propionate with ortho- and meta-methoxybenzaldehyde respectively. *Orthanethoil* (orthopropenylanisoil), $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{CHMe}$, is a liquid with an odour resembling that of veratrole; it boils at $220\text{--}223^\circ$, has a sp. gr. = 1.0075 at 0° , does not solidify at -23° , and readily unites with 2 atoms of bromine.

Metanethoil boils at $226\text{--}229^\circ$; its sp. gr. at 0° is 1.0013, and it also readily combines with 2 atoms of bromine. Orthomethoxyphenylcrotonic acid, m. p. $107\text{--}108^\circ$ (compare Perkin, Trans., 1881, 39, 431, 446 and 449), and *metamethoxyphenylcrotonic acid*, $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{CMe}\cdot\text{COOH}$, may be respectively isolated from the two residues after distilling off the corresponding anethoils in a current of steam. The meta-acid, which is new, crystallises in long, brilliant needles, melts at $92\text{--}93.5^\circ$, and is sparingly soluble in boiling water.

J. J. S.

Dehydrothiotoluidine; Primuline Base. By WILHELM VAUBEL (*J. pr. Chem.*, 1896, [2], 53, 548—549).—The accepted constitution of dehydrothiotoluidine (Abstr., 1889, 867) leads to the expectation that the compound should combine with 2 atoms of bromine, since it contains an amido-group and two unoccupied ortho-positions. As a fact, the addition of a solution of potassium bromide and bromate to a solution of the base in glacial acetic and hydrochloric acids causes the separation of an orange *dibromo-derivative* melting at 184° (uncorr.). Primuline base, however, does not combine, or combines very slowly, with nascent bromine.

A. G. B.

Action of Acid Hydrazides on Acid Azides. By THEODOR CURTIUS and T. S. HOFMANN (*J. pr. Chem.*, 1896, [2], 53, 513—531).—Acid hydrazides generally react with acid azoimides to form symmetrical diacyldihydrazines, hydrogen nitride being eliminated (Abstr., 1894, i, 331); but when the action occurs in boiling acetone, a carbamic acid derivative (a semicarbazide) is the product, and nitrogen is set free. The constitution of the compounds, obtained in this way from benzoylazoimide, is settled by their behaviour on hydrolysis by acids, when they are resolved into aniline salts, carbonic anhydride, a hydrazine salt, and an acid corresponding with the acid radicle.

Phenylbenzoylsemicarbazide, $\text{NHPh}\cdot\text{CO}\cdot\text{NH}\cdot\text{NHBz}$, is prepared by heating for six hours in a reflux apparatus a mixture of benzoylazoimide with benzohydrazide in molecular proportion dissolved in acetone. It forms colourless, lustrous crystals, melts at 212° , and dissolves freely in alcohol and glacial acetic acid, sparingly in hot water, benzene, acetone, and chloroform, but not in cold water. Hydrolysis with acids converts it into aniline, carbonic anhydride, hydrazine, and benzoic acid.

Phenylmetanitrobenzoylsemicarbazide, prepared in like manner from benzoylazoimide and metanitrobenzohydrazide, crystallises in yellowish laminae, melts at 204° , and dissolves in hot glacial acetic acid or hot

alcohol, sparingly in acetone and chloroform, and hardly at all in ether or benzene.

Metanitrophenylbenzoylsemicarbazide, from metanitrobenzoylazoimide and benzohydrazide, is a yellowish, crystalline powder which melts at 226° , and is more sparingly soluble in alcohol than is the last-named compound, although it shows about the same solubility in other solvents. Both these compounds behave normally on hydrolysis (see above).

Phenylacetylsemicarbazide, $\text{NHPh}\cdot\text{CO}\cdot\text{NH}\cdot\text{NHAc}$, is prepared by dissolving 125 grams of benzoylazoimide in acetone, drying the solution over calcium chloride, and adding 100 grams of acetonylacethydrazide dissolved in much acetone; the mixture is boiled in a reflux apparatus for 10 hours, the acetone then evaporated, and the cooled residue dissolved in hot water. The filtered solution, as it cools, deposits the new compound in white laminæ or needles; it melts at 171.5° , and dissolves freely in alcohol, also in hot benzene, acetone, hot chloroform, glacial acetic acid, and hot water. By its hydrolysis, *phenylsemicarbazide*, $\text{NHPh}\cdot\text{CO}\cdot\text{N}_2\text{H}_3$ (isomeric with E. Fischer's compound, Abstr., 1878, 307), may be obtained as an intermediate product; this can be isolated as its benzylidene derivative, which may be subsequently decomposed by boiling hydrochloric acid, the liberated benzaldehyde being extracted by benzene, and the hydrochloric acid solution concentrated to obtain the crystalline phenylsemicarbazide hydrochloride. The base crystallises from hot water in colourless, lustrous laminæ, melts at 122° , and dissolves freely in alcohol, chloroform, and hot benzene, but not in ether; alkalis and acids dissolve it, the latter forming red salts; it reduces Fehling's solution and ammoniacal silver nitrate. The *hydrochlorides*, $\text{NHPh}\cdot\text{CO}\cdot\text{N}_2\text{H}_3\cdot 2\text{HCl}$ and $\text{NHPh}\cdot\text{CO}\cdot\text{N}_2\text{H}_3\cdot\text{HCl}$, are described; the former is reddish, but becomes colourless at 190° , and melts at 213° . The *benzylidene* derivative (m. p. 174°), the *orthohydroxybenzylidene* derivative, and the *cinnamylidene* derivative are described. *Acetonylphenylsemicarbazide*, $\text{NHPh}\cdot\text{CO}\cdot\text{NH}\cdot\text{N}\cdot\text{CMe}_2$, from acetone and phenylsemicarbazide, crystallises in colourless needles, melts at $155\text{--}156^{\circ}$, and dissolves freely in alcohol, acetone, benzene, and chloroform, but only very sparingly in water.

Phenylcarbamazide, $\text{NHPh}\cdot\text{CO}\cdot\text{N}_3$, prepared by diazotising phenylsemicarbazide, crystallises in colourless needles, melts to a red liquid at $103\text{--}104^{\circ}$, and dissolves freely in ether, alcohol, acetone, benzene, and chloroform, but not in water; it is volatile with steam, and has a burning taste; its behaviour with boiling water is described, but requires further investigation.

A prescription for the preparation of acethydrazide in quantity is given in the paper; it melts at 67° (Abstr., 1895, i, 263). *Acetonylacethydrazide* crystallises in white needles and melts at 133° .

A. G. B.

Permanency of Pigments on Cotton-fibre. By V. N. OGLOBIN (*J. Russ. Chem. Soc.*, 1894, 26, 107—136).—A long series of inorganic, organic, and vegetable pigments fixed on cotton fibre has been subjected to the action of sunlight during 366 days with a view of ascertaining the character of the alteration which the pigments

undergo, the part played by oxygen and by moisture in decolorisation, also the effect of the separate rays of the spectrum, and, lastly, the behaviour of the decolorised pigments to different chemical reagents. The results arrived at at present may be summarised as follows: (1) Mineral pigments are the most permanent, except manganic peroxide which is partly bleached after one year. (2) Aniline black is very permanent, remaining unaltered after a year's exposure. (3) The pigments derived from anthracene either remain entirely unaltered after a year's exposure, or acquire a slightly different shade of colour which, however, is very permanent. (4) The rosaniline group is altered by strong sunlight in three days; entirely decolorised in 200 days. (5) The phthaleins and most of the azo-compounds, when applied as pigments, are similarly fugitive, but when developed on the fibre they are much more permanent. (6) Dyes of the diphenylamine series are intermediate in permanency between the anthracene and the rosaniline groups. (7) The permanency of vegetable dyes depends almost entirely on the character of the mordant, and, if well fixed, they rank immediately after the anthracene derivatives in stability.

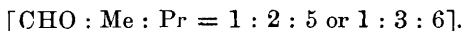
S. G. R.

Preparation of Aldehydes of the Benzene Series. By LOUIS BOUVEAULT (*Compt. rend.*, 1896, 122, 1543—1545).—When glyoxylic acids are heated with aniline at its boiling point, they are converted into phenylimido-acids, which at once decompose into carbonic anhydride and phenylimides.

These phenylimides are very stable, and can be distilled under diminished pressure without decomposing, but when boiled with dilute sulphuric acid, they readily yield aniline and pure aldehydes.

Metaxylylglyoxylic acid yields a phenylimide which boils at about 190° under a pressure of 10 mm. The 2:4-dimethylbenzaldehyde obtained from it boils at 99° under a pressure of 10 mm., yields a hydrazone melting at 114°, and forms 2:4-dimethylbenzoic acid melting at 125°.

Cynylglyoxylic acid, from camphor cymene, yields methylpropylbenzaldehyde, $C_{11}H_{14}O$, which boils at 120° under a pressure of 10 mm., and forms a hydrazone melting at 133°. It has the constitution



Anisoylcarboxylic acid yields anisaldehyde, and veratroylcarboxylic acid yields a phenylimide, which boils at 235° under a pressure of 10 mm., and is readily converted into veratraldehyde (methylvanillin).

The glyoxylic acid from metadimethoxybenzene melts at 106°, its phenylimide boils at 245° under a pressure of 10 mm., and the *meta*-dimethoxybenzaldehyde $[CHO : OMe : OMe = 1 : 2 : 4]$ melts at 66°, and boils at 165° under 10 mm. Paradimethoxybenzene yields dimethylgentisaldehyde, which boils at 146° under 10 mm. pressure, and forms acicular crystals, which melt at 51°.

C. H. B.

Electrolytic Reduction of Benzaldehyde. By H. KAUFFMANN (*Chem. Centr.*, 1896, i, 101; from *Zeits. Elektrotechn. und Elektro-* VOL. LXX. i.

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chemie, 1895, 365—367).—When a solution of benzaldehyde in potassium hydrogen sulphite solution is electrolysed with a current of 0·8 ampère and 6—7 volts, using a platinum cathode of 130 square cm. area, hydrobenzoin and isohydrobenzoin are formed. The same products are obtained when the aldehyde is simply covered with a little aqueous soda and then electrolysed, whereas, in the presence of sulphuric acid, nothing but a tarry mass is formed. A. H.

Action of Hydrazine on the Glyoxylic acids of the Benzene Series. By LOUIS BOUVEAULT (*Compt. rend.*, 1896, **122**, 1491—1493).—The glyoxylic acids react with hydroxylamine, and yield oximes, but when the latter are heated, they lose water, and yield nitriles instead of the oximes of the corresponding aldehydes.

If, however, the sodium salts of the glyoxylic acids are boiled with hydrazine sulphate solution, they yield crystalline yellow acids slightly soluble in boiling water, but almost insoluble in neutral solvents. They all contain H_2O , which they do not lose at 100° , and have the general formula $\text{COOH}\cdot\text{CR}\cdot\text{N}\cdot\text{N}\cdot\text{CR}\cdot\text{COOH} + \text{H}_2\text{O}$. When carefully heated, they lose water at about 150° , and at a higher temperature carbonic anhydride is evolved, decomposition being complete after heating for an hour at 180 — 220° . The hydrazones, $\text{CHR}\cdot\text{N}\cdot\text{N}\cdot\text{CHR}$, thus produced crystallise readily, and are usually yellow. Those derived from the simpler hydrocarbons can be distilled under diminished pressure without decomposing, but if distilled at the ordinary pressure, they all yield nitrogen and substituted stilbenes, and the reaction can be applied to the preparation of various stilbenes.

Sulphuric acid of 15 per cent. has no action on these hydrazones at its boiling point, but when heated in sealed tubes at 140 — 150° , the hydrazones are converted into hydrazine sulphate and aldehydes, the yield, however, is poor.

Phenylglyoxylic acid yields hydrazonephenylglyoxylic acid, which melts and decomposes at 179° with formation of the benzylidenehydrazone described by Curtius. Paracresylglyoxylic acid forms a hydrazone which melts at 200° , and yields the hydrazone of paratolualdehyde; the latter, when distilled under atmospheric pressure, yields paradimethylstilbene. Anisoylglyoxylic acid yields a hydrazone acid, which, in its turn, yields the hydrazone of anisaldehyde, melting at 168° , and a small quantity of an isomeride which dissolves in ether and melts at 152° ; it is the hydrazone of methoxybenzaldehyde. Veratroylglyoxylic acid yields a hydrazone which melts and decomposes at 184° ; the hydrazone of veratraldehyde melts at 190° . C. H. B.

Combination of Antipyrine with the Hydroxybenzoic acids and their Derivatives. By GUSTAVE PATEIN and E. DUEAU (*Compt. rend.*, 1896, **122**, 1335—1338).—Parahydroxybenzoic acid, like salicylic acid, readily combines with antipyrine, forming a compound of the composition $\text{C}_7\text{H}_6\text{O}_3\cdot\text{C}_{11}\text{H}_{12}\text{N}_2\text{O}$, which crystallises from water or alcohol, does not alter when exposed to air, and melts at 78 — 82° . With ferric chloride, it gives the antipyrine reaction. Metahydroxy-

benzoic acid yields an analogous compound, which, however, is liquid.

Sodium salicylate seems to form an unstable compound with antipyrine, but no combination takes place between the latter and methylic salicylate. Anisic acid (paramethoxybenzoic acid) likewise does not combine with antipyrine. Saligenin, on the other hand, yields the compound $C_7H_5O_2 \cdot C_{11}H_{12}N_2O$, which is an oily liquid.

Saligenin is a phenol-alcohol, and from the other known facts concerning the reactions of antipyrine with simple and mixed phenols, the conclusion is drawn that it is the phenolic hydroxyl and not the carboxylic hydroxyl of the hydroxybenzoic acids that determines their combination with antipyrine.

C. H. B.

Dichlorogallic acid and Trichloropyrogallol. By ALEXANDRE BIÉTRIX (*Compt. rend.*, 1896, **122**, 1545—1548).—When an aqueous solution of gallic acid is treated with chlorine, it is completely oxidised, and the chief product is oxalic acid; dibromogallic acid behaves similarly. In presence of alcohol, the reactions are very complex. If, however, the gallic acid is dissolved in about five times its weight of chloroform, and treated with excess of chlorine, it yields dichlorogallic acid, which is insoluble in chloroform, and a small quantity of trichloropyrogallol, which remains in solution.

Dichlorogallic acid crystallises from sulphurous acid in large, white, prismatic crystals very soluble in alcohol or ether, but insoluble in benzene as well as in chloroform. It becomes brown at 180° , and melts and decomposes at 190° . The crystals contain $2H_2O$, and effloresce in a vacuum. Solutions of the acid give a blue coloration with ferric chloride and a rose coloration with alkalis, less intense than that given by dibromogallic acid. Lime water and baryta water give a blue coloration changing to rose.

Trichloropyrogallol crystallises from water in slender needles, which melt and decompose at 178° , and dissolve readily in alcohol and ether. The crystals contain $3H_2O$, which they lose in a vacuum. The triacetyl derivative melts at 125° without decomposing.

C. H. B.

Action of Chlorine on Benzoylnitrocarbazole. By MANFREDO LAMBERTI-ZANARDI (*Gazzetta*, 1896, **26**, 289—293; compare this vol., i, 304).—The benzoylnitrocarbazole, melting at 181° , can be chlorinated in a boiling, dry chloroform solution in presence of iodine, and, after evaporating off the solvent, washing with alkali carbonate, and crystallising from acetic acid, a *benzoylnitrochlorocarbazole*, $C_{15}H_{11}ClN_2O_3$, is obtained, which crystallises in minute, yellow needles melting at 257 — 258° ; it is soluble in benzene or toluene, but only sparingly so in alcohol. It is hydrolysed by boiling alcoholic potash with formation of a *nitrochlorocarbazole*, $C_{12}H_7Cl(NO_2)N$, which crystallises in thin, yellow needles melting at 285 — 286° , and is soluble in toluene or alcohol.

Acetylnitrochlorocarbazole, $C_{12}H_6Cl(NO_2)N \cdot Ac$, is obtained by heating nitrochlorocarbazole with acetic anhydride at 170 — 180° for six hours; it crystallises in white needles melting at 205 — 206° .

W. J. P.

Action of Ethyloxalic Chloride [Ethylic Chloroglyoxylate] on Naphthalene in the presence of Aluminium Chloride. By L. ROUSSET (*Compt. rend.*, 1896, **123**, 60—62; compare Bouveault, this vol., i, 551, 616).—Ethylic chloroglyoxylate reacts with naphthalene in the presence of aluminium chloride to form a mixture of ethylic α - and β -naphthylglyoxylates; these are best separated by treating a solution of the two in methylic alcohol with picric acid, the α -glyoxylate uniting with the picric acid to form a definite compound, which crystallises in yellow needles, and melts at 77°. When decomposed with sodium carbonate, this picrate yields *ethylic α -naphthylglyoxylate*; this is a viscid liquid, boiling at 213—215° under a pressure of 23 mm., and having a sp. gr. = 1.19 at 0°. On hydrolysis it yields *α -naphthylglyoxylic acid*, which readily crystallises from benzene; these crystals, which contain benzene, turn brown at 95° and melt at 100°; when free from benzene, the acid melts at 107—108°. Compare Claus and Feist (Abstr., 1887, 271), who give the melting point of the acid as 113.5°. The acid yields an *oxime* melting and decomposing at 193—195°; this when distilled under diminished pressure, decomposes, yielding *α -naphthonitrile*, which melts at 34°, boils at 170—175° under a pressure of 20 mm., and yields a *picrate* melting at 97°.

Ethylic β -naphthylglyoxylate boils at 212—215° under a pressure of 20 mm.; its sp. gr. at 0° = 1.18. No pure derivatives could be obtained.

The two naphthylglyoxylic acids, when heated with aniline, yield phenylimides, and these, when boiled with dilute sulphuric acid yield the naphthoic aldehydes, which have already been described by Bamberger and Lodter (Abstr., 1888, 375), Battershall (*Annalen*, 1883, **168**, 116), Schulze (Abstr., 1884, 1184), and Bamberger and Böckmann (Abstr., 1887, 675).
J. J. S.

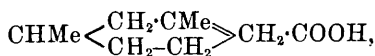
Camphorpinacone. By ERNST BECKMANN [and AUG. STOCK] (*Annalen*, 1896, **292**, 1—30; compare Abstr., 1894, i, 614).—Camphorpinacone, $C_{20}H_{34}O_2$, crystallises in pyramids belonging to the rhombic system; $a : b : c = 0.9573 : 1 : 1.1035$. It melts at 157—158°, is odourless and tasteless, and is very slightly volatile in an atmosphere of steam; in a solution containing 23 grams of the pinacone in 100 grams of benzene, the specific rotatory power $[\alpha]_D = -27.3^\circ$.

Whilst the foregoing substance is obtained from dextro-camphor, reduction of lævo-camphor gives rise to an *isomeride* which, in benzene solution, has the specific rotatory power $[\alpha]_D = +26.5^\circ$.

The author describes in some detail the substances already enumerated (*loc. cit.*), and develops a system of nomenclature applicable to them; the constitution of the more prominent compounds is also discussed.
M. O. F.

Constitution of Inactive Campholenic acid. By GUERBET and AUGUSTE BÉHAL (*Compt. rend.*, 1896, **122**, 1493—1496).—When heated in a sealed tube with bromine, inactive campholenic acid yields Claus' metaxylylacetic acid (Abstr., 1890, 979) which, however, melts at 106°, boils at 300—302° (corr.), and yields an amide melting at 183°

It follows that campholenic acid is tetrahydrodimethyl-1 : 3-phen-
ethyloic-4-acid (tetrahydropseudocumenecarboxylic acid)



though there is some uncertainty as to the position of the ethylenic grouping. This view is inconsistent with the results of the oxidation of campholenic acid (this vol., i, 55, 179), although it agrees well with all other transformations (Abstr., 1895, i, 240, 241, 552, 623). It is, however, known that in several instances oxidation is accompanied to some extent by molecular transformations, and it seems probable that such changes take place in the oxidation of campholenic acid. Since this acid contains an ethylenic group, it may possibly be first converted into a pinacone, which is converted into a pinacolone, the latter being subsequently oxidised with transposition of a methyl group.

C. H. B.

Camphoronic acid. By JULIUS BREDT [and in part E. AKNTZ and ALFRED HELLE] (*Annalen*, 1896, **292**, 55—132; compare Abstr., 1895, i, 242).—The author states that camphoronic acid melts at 136—137°, and confirms the observation of Hess (this vol., i, 102); anhydro-camphoronic acid melts at 139°, and crystallises in the rhombic system, $a : b : c = 0.96887 : 1 : 0.80866$.

The paper is devoted to a detailed account of derivatives of camphoronic acid already described (Abstr., 1895, i, 242), and the author discusses the question of constitution at considerable length.

M. O. F.

Red Pigment from Amanita muscaria. By ARTHUR B. GRIFFITHS (*Compt. rend.*, 1896, **122**, 1342).—The red pigment of *Amanita muscaria* (*Agaricus muscarius*) is amorphous, and soluble in chloroform and ether, but does not dissolve in water. Its solutions show no characteristic absorption bands. It has the composition $\text{C}_{19}\text{H}_{18}\text{O}_6$, and the author calls it provisionally *amanitin*.

C. H. B.

Cardol. By LEOPOLD SPIEGEL and CARL DOBRIN (*Chem. Centr.*, 1896, i, 112; from *Ber. Pharm. Ges.*, **5**, 309—325).—The composition of different preparations of cardol corresponds with the formula $\text{C}_{32}\text{H}_{50}\text{O}_3$ or $\text{C}_{32}\text{H}_{52}\text{O}_4$; the specimens which give the latter formula, however, lose H_2O when heated, so that the former of the two is the true formula. Cardol does not react with hydroxylamine, but yields a monacetyl derivative, and forms compounds with alkalis. When treated with sodium in boiling amyl alcohol, it is reduced to a brown viscid mass, which has the formula $\text{C}_{32}\text{H}_{52}\text{O}_2$. On distillation with zinc dust, it yields *cardene*, C_8H_8 , which boils at 122—127°, and is not identical with styrene. Concentrated nitric acid converts cardol into a nitrogenous substance, $\text{C}_{30}\text{H}_{52}\text{NO}_{12}$, melting at 105°, the dibasic *cardolic acid*, $\text{C}_{15}\text{H}_{28}\text{O}_7$, which melts at 120°, being also formed. When the insoluble portion of the oxidation product is treated with potassium permanganate, it yields *cardic acid*, $\text{C}_{13}\text{H}_{24}\text{O}_5$, melting at 89°. The direct oxidation of cardol with potassium permanganate yields the monobasic *cardenic acid*, $\text{C}_{16}\text{H}_{30}\text{O}_7$, melting at 126°. The yellow mass formed by the action of

nitric acid is reduced by tin and acetic acid to a paraffin-like substance, $C_{15}H_{34}O_2$, melting at 59° .

These results show that cardol is not in any way related to cantharidin, and the authors have found that the cantharidin-like effects of acajou balsam are in reality due to a substance which is soluble in ether, and not to cardol itself.

A. H.

2 : 4 : 1-Dinitrohydroxyquinoline. By ADOLPH CLAUS and EMIL DEWITZ (*J. pr. Chem.*, 1896, [2], **53**, 532—548).—2 : 4 : 1-Dinitrohydroxyquinoline, prepared by nitrating 1-hydroxyquinoline in glacial acetic acid, is a yellow, crystalline powder, decomposes at 276° when heated in a capillary tube, and is insoluble in the usual solvents, but dissolves in hot alkalis and concentrated acids. The *potassium* salt, with $\frac{1}{2}H_2O$, *sodium* salt, with $\frac{1}{2}H_2O$, *ammonium* salt, and *copper* salt, with $1H_2O$, are described, also the double salts, $C_9NH_4(NO_2)_2 \cdot OK + 2BaCl_2 + 3H_2O$; $C_9NH_4(NO_2)_2 \cdot OK + 2CaCl_2 + 6H_2O$; $4C_9NH_4(NO_2)_2 \cdot OK + AgNO_3$ (with $\frac{1}{2}H_2O$?), and $C_9NH_4(NO_2)_2 \cdot OK + Pb(NO_3)_2$. Attempts to prepare alkylic ethers from the alkali salts have failed. Salts in which the dinitrohydroxyquinoline has a basic function cannot be isolated, although they appear to exist; the *platinochloride* is of the irregular composition $[C_9NH_4(NO_2)_2 \cdot OH]_2, 2H_2PtCl_6$.

2 : 4 : 1-Diamidohydroxyquinoline is obtained by reducing the dinitro-compound with tin and hydrochloric acid; the stannichloride formed must be decomposed by hydrogen sulphide, since alkalis cause a deeply seated change. The *hydrochlorides*, $C_9H_8N_3O \cdot 3HCl$ and $C_9H_8N_3O \cdot 2HCl$, are brown and red respectively. The free base, isolated by adding excess of sodium carbonate to the solution of the hydrochloride and extracting with chloroform, is a red crystalline powder, soluble in the usual solvents. The *platinochloride*, $C_9H_8N_3O \cdot H_2PtCl_6$, is described. The *diacetyl* derivative,



crystallises in yellow needles, and melts and decomposes at 240° ; the corresponding *dibenzoyl* derivative melts at 263 — 264° , and sublimes unchanged.

2 : 4-Diamidoquinoline is prepared by heating the diamidohydroxyquinoline hydrochloride with hydriodic acid, iodine, and red phosphorus in a reflux apparatus. The *hydriodide*, $C_9H_8N_3 \cdot 2HI$, crystallises in red needles, melts at 215 — 216° , and dissolves in water and alcohol; the *platinochloride*, $C_9H_8N_3 \cdot H_2PtCl_6$, is described. The base is identical with that obtained by reducing 2 : 4-dinitroquinoline (this vol., i, 392).

2 : 4 : 1-Dinitramidquinoline is prepared by heating 2 : 4 : 1-dinitrohydroxyquinoline with alcoholic ammonia at 180° for 3—4 hours; it crystallises in yellow needles, melts in a capillary tube at 187 — 188° , and dissolves in most organic solvents. It is remarkable that this compound has so little basic tendency that it does not even form a platinochloride. By reduction with stannous chloride and hydrochloric acid, it yields 1 : 2 : 4-triamidoquinoline, which forms red-brown crystals, and does not melt at 350° ; the *hydrochloride*, $C_9H_{10}N_4 \cdot 3HCl$, is described.

A. G. B.

"Quinine Chlorhydro-sulphate." By GEORGES (*J. Pharm.*, 1896, **3**, 589—594).—A pharmaceutical preparation of quinine used in France. A careful chemical, microscopical, and polarimetric investigation has proved it to be a mixture of quinine sulphate and quinine hydrochloride. L. DE K.

Ketones of the Tropine Group. IV. ψ -Tropigenine. By RICHARD WILLSTÄTTER (*Ber.*, 1896, **29**, 1636—1639; compare this vol., i, 327, 451, 582).—When nortropinone carbamate is reduced by means of sodium and ethylic alcohol, ψ -tropigenine is produced. The base is obtained as an oil, and is best purified by converting it into the carbamate; this is a crystalline powder, which is non-hygroscopic, but dissolves readily in water, and melts at 138—140°, carbonic anhydride being evolved; its solution does not yield precipitates with picric acid or with cold calcium chloride, but the latter, when hot, gives an immediate deposit. The free base, $C_7H_{13}NO$, is precipitated in slender needles on adding strong soda to the carbamate; it is readily soluble in water and alcohol, but only sparingly in ether; when exposed to the air, it absorbs aqueous vapour and carbonic anhydride. The aurochloride, $C_7H_{13}NO, HAuCl_4$, is obtained as a dense, orange-yellow, crystalline precipitate, soluble in alcohol and in hot water; it crystallises in fern-like leaflets composed of aggregated prisms, and melts and decomposes at 211—212°. The platinochloride, $(C_7H_{13}NO)_2, H_2PtCl_6$, crystallises from hot water in anhydrous, shining, red leaflets consisting of aggregations of prisms; it is insoluble in alcohol, and melts and decomposes at about 240°. The benzoyl derivative, $C_7H_{12}ONBz$, is more readily soluble in hot water than in cold, and dissolves easily in acetone; it crystallises from water in well defined, highly refractive, rhombic tables, and from alcohol in colourless, shining needles; it melts at 165—166°. The properties of the foregoing compound are very distinct from those of the benzoyl derivative of tropinein. A. L.

The Identity of Methylprotocotoin and Methylhydrocotoin with the Corresponding Compounds obtained by Ciamician from Leucotin. By GIOV. B. NEGRI (*Chem. Centr.*, 1896, i, 311—312; from *Rivista di Min. e Crist.*, **13**, 85).—The supposition of Ciamician and Silber (*Abstr.*, 1893, 417), that the leucotin of Jobst and Hesse is a mixture of methylprotocotoin and methylhydrocotoin, is confirmed, the author having found that the crystallographic constants are identical with those of the pure compounds. Methylprotocotoin forms tablets, which are probably monoclinic, and have an angle of extinction of about 26°. Methylhydrocotoin is also monoclinic, the axial ratio being 1.9913 : 1 : 0.5663, and the angle $\beta = 58^\circ 41'$.

A. H.

Scopolamine and Atroscine. By OSWALD HESSE (*Ber.*, 1896, **29**, 1776—1785).—The identity of scopolamine and hyoscine has been fully proved by various observers, but Rachlmann states that, physiologically, scopolamine from *Scopolia* root is superior to hyoscine from *hyoscyamus*; as this statement is confirmed by others, the latter preparation must contain a new alkaloid. The author has

succeeded in isolating this compound, which he terms *atroschine*, by the fractional crystallisation of anhydrous commercial "scopolamine" hydrobromide from alcohol (97 per cent.), in which the *atroschine* salt is less soluble. The base, $C_{17}H_{21}O_4N$, is amorphous, melts at about 50° , and is alkaline to litmus paper, but is without effect on phenolphthaleïn. It is isomeric with *hyoscine*, with which it appears to form a racemic compound. By the action of water at 10° , *atroschine* forms a hydrate with $2H_2O$, which crystallises in colourless, concentric needles, melting at $36-37^\circ$. With potash, it is decomposed, like *hyoscine*, into *oscine* and, probably, *tropic acid*, but the latter is at once converted into *atropic acid*. The *hydrochloride* crystallises in long, colourless needles, and is optically inactive. No *platinochloride* could be prepared; the *aurochloride* crystallises in small, yellow plates, melting at $201-202^\circ$, and decomposing at $204-206^\circ$; at 50° , it dissolves in 690 parts of dilute hydrochloric acid (1 per cent.). The *hydrobromide*, $C_{17}H_{20}O_4N \cdot HBr + \frac{1}{2}H_2O$, crystallises from alcohol in short, rhombic prisms, and from water in large, glassy, rhombic plates; in solubility, it resembles the *hyoscine* salt, but is optically inactive. The *hydriodide* forms colourless, short, concentric prisms. Attempts to convert *atroschine* into *hyoscine* by the action of alkalis, or silver oxide, were unsuccessful; either the alkaloid decomposed as with potash (see above) or no action took place. The amount of *atroschine* hydrobromide in commercial *hyoscine* hydrobromide is readily determined by means of the refractive power; the former compound is inactive, but for the latter, $[\alpha]_D = -22.5^\circ$. *Atroschine* causes dilation of the pupil to the same extent as *atropine*, but its general effect on the system is less marked; its action on accommodation both in extent and duration is 2-4 times as great as that of *atropine* and *scopolamine*. E. Schmidt has recently suggested that *atroschine* is identical with *i*-*scopolamine*, but a comparison of the bases, hydrobromides, and aurochlorides, shows that this is not the case; as *i*-*scopolamine* is feebly *lævogyrate*, and the hydrobromide feebly *dextrogyrate*, *i*-*scopolamine* is probably a mixture of *atroschine* and a new *dextrogyrate* alkaloid. The author suggests that the name *scopolamine* should no longer be used.

J. B. T.

Hyoscine. By OSWALD HESSE (*Ber.*, 1896, **29**, 1771-1776).—Ladenburg's paper on this subject (*Abstr.*, 1893, i, 739) is first discussed. The author maintains the accuracy of his formula, $C_{17}H_{21}O_4N$, for *hyoscine*, and Ladenburg's analyses, made with fully purified materials, are in better agreement with the author's than his own formula, $C_{17}H_{23}O_3N$.

When a mixture of *tropine* and *oscine*, in hydrochloric acid solution, is treated with platinic chloride, *tropine* *platinochloride* is first deposited in small crystals, which have been described by von Lasaulx; if these are allowed to remain in contact with the mother liquor, they disappear, and large, orange-red prisms are formed having the same composition as the former; they appear to be identical with the *pseudotropine* *platinochloride* crystals described by Milch. The *oscine* salt is only deposited when the mother liquor is considerably concentrated. If, in the above experiment, gold chloride is substi-

tuted for platinic chloride, oscine aurochloride is deposited first. These facts probably account for Ladenburg's erroneous observations.

Hyoscine forms two very characteristic salts, the aurochloride and hydrobromide. The former crystallises in long, yellow, slightly lustrous plates, melts and decomposes at 198—199°, and at 50° dissolves in 510 parts of dilute hydrochloric acid containing 10 parts of acid (sp. gr. = 1.19) per litre. The hydrobromide is deposited with 3H₂O in large, vitreous, rhombic crystals, melting at 100° in their water of crystallisation, $[\alpha]_D = -25.7^\circ$; the anhydrous compound melts at 181°. If the anhydrous salt is recrystallised from alcohol (95 per cent.), colourless, rhombic prisms with 2H₂O are formed; from absolute alcohol, anhydrous rhombohedra are obtained. By the action of potash, hyoscine is liberated and quickly decomposed into tropic acid and oscine, the former then slowly changes into atropic acid. It has been previously stated by the author that another alkaloid of lower refractive power is formed under these circumstances, but this is not the case. Sodium, barium and calcium hydroxides act like potash; silver oxide and ammonia liberate hyoscine, which undergoes no further change. J. B. T.

The Alkaloids of *Anagyris Foetida*. By ALFRED PARTHEIL and L. SPASSKI (*Chem. Centr.*, 1896, i, 375; from *Apoth. Zeit.*, 10, 903—904).—The commercial product known as "*Anagyrinum hydrobromicum*" appears to be a mixture of substances. The seeds of *Anagyris foetida* contain two alkaloids, cytisine and anagyrine. The aqueous solution of the latter is laevorotatory, and its *aurochloride* melts at 206—207°. Doubt is cast by the authors on the various formulæ which have been proposed for anagyrine. A. H.

Synthesis of Cytisine. By JOH. VAN DE MOER (*Chem. Centr.*, 1896, i, 312; from *Nederl. Tijdschr. Pharm.*, 7, 362—365).—Cytisine is *apopilocarpine*, and, since pilocarpine belongs to the γ -series, it is probable that cytisine is also a γ -compound. The author is investigating the question experimentally. A. H.

Gelseminine. By M. GÖLDNER (*Chem. Centr.*, 1896, i, 111; from *Ber. pharm. Ges.*, 5, 330—359).—The author has repeated Spiegel's work on gelseminine (*Abstr.*, 1893, i, 492), and confirms his results, so that the statements of Cushny (*Abstr.*, 1893, i, 614) must be considered as erroneous. *Gelsemininemethylammonium hydroxide* melts at 203°. When gelseminine methiodide is distilled with solid potash, four different substances are obtained under varying conditions; a base of the formula C₁₅H₂₄NO₅ or C₁₅H₂₂NO₄, the *hydrochloride* of which melts at 265°; a *hydrochloride* of the formula C₂₁H₂₉N₃O₅.HCl, which melts at 286°; a salt of the composition C₁₀H₁₁N.HCl, melting at 303°; and, finally, a resinous substance of the composition C₁₀H₁₃N, which is not identical either with tetrahydrotoluquinoline (ortho- or para-) or with tetrahydroisoquinoline. Gelseminine yields a *monacetate* melting at 290°, and a *monobenzoate* melting at 303°. Oxidation with potassium permanganate yields a compound melting at 238°, the empirical formula of which is C₁₅H₁₉N₂O₉. A. H.

Nucleic and Thymic acids. By ALBRECHT C. L. M. L. KOSSEL and ALBERT NEUMANN (*Zeit. physiol. Chem.*, 1896, **22**, 74—81).—The acid discovered in egg-yolk by Altmann is not nucleic acid, as the decomposition products of the latter cannot be obtained from that source.

Nucleic acid is decomposed by hydrolysis into thymic acid, adenine, guanine, and cytosine (compare Abstr., 1894, i, 156). The decomposition is effected in the following manner: 10 grams of nucleic acid is boiled with 500 c.c. of water until addition of hydrochloric acid causes no precipitate of unaltered nucleic acid; the filtered liquid is then made faintly alkaline with baryta water, and allowed to remain one day, when guanine and barium carbonate are precipitated, adenine, cytosine, and barium thymate remaining in solution. The barium thymate is then precipitated by the addition of alcohol, whilst the adenine and cytosine are separated by means of their silver compounds, that of adenine being insoluble in water. The barium thymate is purified by washing, dissolving it in water, and precipitating with alcohol; the addition of barium chloride to the liquid in the latter instance ensures complete precipitation.

Barium thymate, $C_{16}H_{23}N_3P_2O_{12}Ba$, contains water of crystallisation, which it slowly loses at 100° ; it dissolves readily in water, and, when anhydrous, is excessively hygroscopic. Thymic acid differs from the parent nucleic acid by its ready solubility in water and dilute mineral acids, the precipitates it yields with albumin or propeptone being also more readily soluble in hydrochloric acid than those afforded by nucleic acid. Nucleic acid does not behave as an acid salt of thymic acid, for when it is dissolved in barium hydroxide and the barium salt is precipitated by alcohol, no nuclein bases can be detected in the liquid, whilst adenine or guanine thymate when subjected to similar treatment at once give evidence of the production of free base.

A. L.

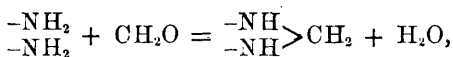
Formation of a Pyridine Derivative from Albumin by boiling with Hydrochloric acid. By RUDOLPH COHN (*Ber.*, 1896, **29**, 1785—1789).—Casein (1 kilo.), when boiled during five hours with concentrated hydrochloric acid (sp. gr. = 1.9, 3 litres), yields tyrosine, leucine, carbonic anhydride, and ammonia in small quantity; aspartic acid, and glutamic acid, in comparatively large quantity a compound which yields iodoform, an oily acid which is still under investigation, and a pyridine derivative, probably C_5H_7ON ; the latter is separated from the leucine by means of sulphuric acid. It is sparingly soluble in water, crystallises in long, feathery needles, melts at 296° , and readily sublimates; when quickly heated, it decomposes, acid vapours being evolved; it is not changed by alkalis or acids, dilute or concentrated. No salts could be prepared. When distilled with zinc dust in an atmosphere of hydrogen, pyridine is formed. The yield of crude substance is about 0.6 per cent. of the casein employed.

J. B. T.

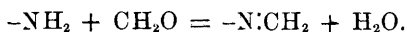
New Series of Proteids. By F. BLUM (*Zeit. physiol. Chem.*, 1896, **22**, 127—131).—If white of egg is diluted with water, and after being filtered from globulins, a little formaldehyde is added to the

solution of ovomucoid and egg albumin, the latter is found to have lost its power of coagulating. The liquid is then distilled until neither the residual liquors nor the distillate give the aldehyde reaction with decolorised magenta; it now has a faintly sweet taste, and an odour of fresh egg-albumin, and when evaporated on the water bath deposits a pellicle of albuminous matter.

The dried albumin is transparent, bright yellow, and readily soluble in water, and in solution of sodium chloride or sulphate. It is precipitated from its solution by mineral acids, absolute alcohol, or acetone; the solution also gives characteristic precipitates with potassium ferrocyanide, tannin, and salts of the heavy metals; violet and red coloration being produced on the addition of alkaline copper solution or mixed acetic and sulphuric acids. When precipitated by acetone, it may be subsequently dissolved by the addition of a few drops of water. It gives the xanthoprotein and Millon's reactions, and a precipitate of lead sulphide is formed when it is boiled with alkaline lead acetate. Its behaviour is unlike that of any known albumin, and its production by the interaction of formaldehyde may possibly be represented thus,



or,



A. L.

Decomposition Products of Proteids. By SVEN G. HEDIN (*Zeit. physiol. Chem.*, **22**, 191—196).—As has been shown by Drechsel, albumins, when heated with hydrochloric or phosphomolybdic acid, yield a mixture of bases. From the latter, the author has already isolated arginine, whilst, from the precipitates they yield with silver nitrate, Siegfried has obtained a new base in the form of its hydrochloride, $\text{C}_{11}\text{H}_{20}\text{N}_6\text{O}_6 \cdot 2\text{HCl}$ (see Abstr., 1891, 591).

In the present paper, the author describes the results of his investigation of this silver precipitate; the latter is decomposed by hydrogen sulphide, and the aqueous solution of the product is mixed with ammoniacal lead acetate, when a small quantity of a compound containing sulphur is precipitated. The filtrate is then freed from lead, and mixed with ammoniacal silver nitrate, the precipitate formed being decomposed by hydrochloric acid, and the filtered solution evaporated nearly to dryness. The *hydrochloride* of the new base separates in beautiful tables of the composition $\text{C}_6\text{H}_9\text{N}_3\text{O}_2 \cdot \text{HCl} \cdot \text{H}_2\text{O}$; it is optically inactive, somewhat readily soluble in water, but insoluble in alcohol and ether; its aqueous solution has an acid reaction.

The free base, $\text{C}_6\text{H}_9\text{N}_3\text{O}_2$, crystallises from water in the form of needles or tables. Its aqueous solution has a feeble alkaline reaction, and does not absorb carbonic anhydride; it gives no precipitate with neutral silver nitrate, but on the addition of ammonia a *silver compound*, $\text{Ag}_2\text{C}_6\text{H}_9\text{N}_3\text{O}_2 \cdot \text{H}_2\text{O}$, is obtained as a voluminous, amorphous precipitate readily soluble in alcohol.

The above base is possibly identical with that of Siegfried; it appears, also, to be identical with Kossel's histidine, $\text{C}_{12}\text{H}_{16}\text{N}_6\text{O}_4$ (see this vol., i, 582), as, although the properties of the hydrochloride, as

described by that author, are not in accordance with those of the foregoing salt, the crystals of both have been goniometrically measured, and the results are practically identical. A. L.

The Behaviour of Casein towards Pepsin-hydrochloric acid.

By ERNST L. SALKOWSKI (*Pflüger's Archiv*, 1896, **63**, 401—422).—Several recent writers have shown that casein, unlike other nucleo-proteids, yields a nuclein which is largely soluble on gastric digestion. The present experiments show that casein is wholly soluble in pepsin-hydrochloric acid; the conclusions as to the conditions under which this occurs are the following: complete solution occurs if the presence of dry, hard lumps of casein is excluded; this may be done by making a solution of the casein before adding the digestive mixture, which should be present in the proportion of 500 to 1 of casein. If the proportion is 250 to 1, about 1 per cent. of the casein remains undissolved; the residue increases with smaller proportions. The percentage of hydrochloric acid, which is best, is between 0.054 and 0.216; within these limits, difference in amount of digestion does not occur; above the higher limit, digestion is slightly impeded.

W. D. H.

Phycocyanin, a Crystallisable Proteid.

By HANS MOLISCH (*Chem. Centr.*, 1896, i, 111—112; from *Bot. Zeit.*, 1895, i, 131).—The colour of the blue-green algæ or cyanophyceæ is due to chlorophyll, phycoxanthin, and phycocyanin. A solution of the last of these, obtained from *Oscillaria leptotricha* (Kütz.), was obtained in crystals by salting out its solution with ammonium sulphate. It has not yet, however, been decided whether the crystals consist of pure phycocyanin. A. H.

Preparation and Composition of Hæmine Hydrochloride.

By M. CLOETTA (*Chem. Centr.*, 1896, i, 260; from *Arch. exp. Path. Pharm.*, **36**, 349—360).—Coagulated blood is freed from serum, washed with sodium sulphate solution, and finally with strong alcohol. The mass is then powdered, dried, and ground up with 96 per cent. alcohol and a few drops of concentrated sulphuric acid; a little alcoholic hydrochloric acid is added to the boiling filtrate, and the whole allowed to cool. Hæmine hydrochloride separates in fascicular groups of long, pointed needles, which have a dark violet colour and a metallic lustre. Alkalis precipitate hæmine as an amorphous, black-brown powder. The recrystallised hydrochloride appears to have the composition $4(C_{30}H_{34}N_3FeO_3 \cdot HCl) + C_{20}H_{34}N_3FeO_3$. It seems probable that the specimens analysed by Hoppe-Seyler, who gave to hæmine the formula $C_{34}H_{31}N_4FeO_3 + 2H_2O$, and by Küster and Nenki and Sieber, who arrived at the formula $C_{32}H_{30}N_4FeO_3$, contained xanthine. A. H.

Phosphocarnic acid.

By MAX A. SIEGFRIED (*Zeit. physiol. Chem.*, 1895, **21**, 360—379).—This paper gives full details of the researches on carniferin, phosphocarnic acid, and carnic acid, short notices of which have been already published (see Abstr., 1895, i, 76 and 313).

A. L.

Organic Chemistry.

Preparation of Cyanogen Bromide. By JOSEPH TCHERNIAC (*Ber.*, 1896, **29**, 2078—2079).—A polemical paper replying to Scholl's criticisms (this vol., i, 585). J. J. S.

Alcoholic Hydrates. By H. P. BARENDRECHT (*Zeits. physikal. Chem.*, 1896, **20**, 234—241).—Considering the question of the existence of alcoholic hydrates to be in an unsettled state, the author endeavoured to obtain solid hydrates by cooling alcoholic solutions of various strengths. In the more dilute solutions, well-defined, six-sided crystals were obtained at -40° ; these, on analysis, were found to contain 37 per cent. of ethylic alcohol, and hence are not the supposed hydrate, $C_2H_6O, 3H_2O$, which should contain 46 per cent. (*Abstr.*, 1894, ii, 374), but are considered by the author to be merely ice crystals. In 75 per cent. alcohol, a second form of crystal was obtained, cubic and isotropic. These crystals are probably also crystals of ice, the dimorphism of which has been previously stated, and this view is supported by the fact that similar crystals are formed in mixtures with other alcohols or with aldehyde. The author concludes, therefore, that no solid hydrates are formed under these conditions, and that the existence of such compounds in solution is very improbable. L. M. J.

Crotonylic Alcohol and its Ethereal Salts. By ER. CHARON (*Compt. rend.*, 1896, **123**, 250—252).—In the reduction of crotonaldehyde, the proportion of pinacone formed is unusually high, and amounts to 60 per cent. of the total product. Normal butaldehyde occurs amongst the products, but the corresponding alcohol is not formed, a result which is due to the fact that the zinc-copper couple has no action on saturated aldehydes. It also has no action on crotonylic alcohol. In the reduction of crotonaldehyde by the couple, a small quantity of butaldehyde is formed, but is not further reduced, and a larger quantity (about 25 per cent. of the total product) of the corresponding unsaturated alcohol is produced, and is likewise stable under the conditions of the experiment, the ethylenic grouping remaining unattacked. Paracetaldehyde was found in notable quantity amongst the products, but it most probably pre-existed as an impurity in the crotonaldehyde.

The products of the reduction of crotonaldehyde do not vary appreciably under somewhat wide variations in the dilution of the liquid or in the temperature at which reduction takes place, but a temperature of 0° seems to favour the production of glycol. The process of reduction results in the development of much heat.

The ethereal salts of crotonylic alcohol are readily obtained by the action of the acids or anhydrides, but not by the action of acid chlorides. The *formate* is a crystallisable compound which boils at 112° , sp. gr. = 0.9301 at 0° ; the *acetate* boils at $130-131^{\circ}$, sp. gr. = 0.9338 at 0° ; the *propionate* boils at $150-151^{\circ}$, sp. gr. = 0.9339 at

0°; the *isobutyrate* boils at 158—159°, sp. gr. = 0.9067 at 0°; the *isovalerate* boils at 178—179°, sp. gr. = 0.9012 at 0°.

The action of acid chlorides on the alcohol yields a somewhat complex mixture containing several isomerides. C. H. B.

Preparation of Diallylethyl Alcohol. By ERWIN OBERREIT (*Ber.*, 1896, **29**, 2005—2007).—*Diallylacetamide* is obtained by heating ammonium diallylacetate at 230—260°; it crystallises in long needles, melts at 82.5°, and boils at 265°. *Diallylacetoneitrile* is an oil, boiling at 186—188°, and has a pleasant smell and sweet taste. When this is treated in alcoholic solution with sodium, it is converted into *diallylethylamine*, an unpleasant smelling, caustic liquid, which boils at 167°, unites with moisture from the air, has an alkaline reaction, and fumes with hydrochloric acid. The *hydrochloride* is excessively hygroscopic; the *platinochloride* is sparingly soluble. When the hydrochloride is treated with silver nitrite, the stable *nitrite* of the base is formed; at 80°, however, this decomposes, with evolution of nitrogen and production of *diallylethyl alcohol*, which boils at 170—173°, and is not miscible with water. A. H.

Constitution of Pinacolin. By MAURICE DELACRE (*Compt. rend.*, 1896, **123**, 245—248).—The author continues the discussion of the constitution of pinacolin (this vol., i, 591; see also Abstr., 1893, i, 244). When pinacolic alcohol is treated with gaseous hydrogen iodide, it yields tetramethylethylene and a small quantity of a liquid which boils below 70—73°, and this, when converted into a bromide and treated with alcoholic potash, seems to yield a small quantity of an acetylenic hydrocarbon. The author considers that the identity of pinacolin with the product obtained by Boutlerow has never been definitely established. The ketone obtained by Boutlerow's method boils at about 105°, and has an odour distinctly different from that of pinacolin, although similar to it. When hydrogenised, it yields an alcohol which boils at 118° but does not solidify in a mixture of sodium sulphate and hydrochloric acid, and is therefore not identical with pinacolic alcohol. When heated with hydrogen iodide, this alcohol yields tetramethylethylene; its other properties remain to be investigated.

When Boutlerow's ketone is treated with $3\frac{1}{2}$ times its weight of concentrated hydrobromic acid, heat is developed, and the two liquids mix perfectly, but the mixture remains limpid and retains its pale straw colour for many hours. Pinacolin under the same conditions becomes almost black, and very soon forms an abundant precipitate.

C. H. B.

Action of Sulphur Chloride on Penterythritol. By J. BOUGAULT (*Compt. rend.*, 1896, **123**, 187—189).—When penterythritol (*Abstr.*, 1892, 127) is boiled with five times its weight of sulphur chloride until evolution of hydrogen chloride ceases, it yields a mixture of *penterythritol bisulphite*, $C_5H_8(SO_3)_2$, and *penterythritol dichlorhydrin*, $C_5H_8Cl_2(OH)_2$. The bisulphite crystallises from boiling alcohol in bulky, rhomboidal lamellæ, which melt at 153—154°, and sublime without decomposing. It is almost insoluble in water, and only

slightly soluble in common organic solvents at the ordinary temperature, but dissolves somewhat readily at their boiling points. It has a neutral reaction, and does not change when boiled with water, but in presence of a trace of acid it is partially decomposed. When boiled with aqueous potash, it is completely converted into potassium sulphite and penterithritol. Dry hydrogen chloride has no action on the compound at its melting point.

Penterithritol dichlorhydrin can be crystallised from ether or benzene, and forms monoclinic crystals, $a : b : c = 0.8210 : 1 : 0.6338$, and $\beta = 84^\circ 4'$. It melts at 65° , and boils at $150\text{--}155^\circ$ under reduced pressure. It is soluble in water, very soluble in alcohol and ether, less soluble in benzene and chloroform, insoluble in carbon bisulphide. When boiled with aqueous potash, it is completely converted into penterithritol.

The bisulphite is not affected by boiling sulphur chloride, and hence it would seem that the formation of the two compounds is simultaneous, and is probably represented by the equation



Mixed Aliphatic Secondary Amines. By RICHARD STOERMER and VICTOR VON LEPEL (*Ber.*, 1896, **29**, 2110—2121; compare this vol., i, 275 and 298).—*Methylpropylamine* is a colourless liquid of ammoniacal, fish-like odour, has a sp. gr. = 0.7204 at 17° , and boils at $62\text{--}64^\circ$; it is very hygroscopic, and, being very volatile at ordinary temperatures, burns with a luminous flame when ignited. It is prepared from methylpropylaniline, which is converted into the nitroso-derivative, and the hydrochloride heated with a 10 per cent. solution of soda, the base being collected in concentrated hydrochloric acid, which is then evaporated to dryness and treated in the same way. The *hydrochloride* crystallises in white, deliquescent scales; the *platinochloride* in red needles, which decompose and melt at 200° ; the *aurochloride*, which is readily reduced, crystallises in long, yellow needles. The *carbamide* and *phenylcarbamide* melt at 95° and 89° respectively, whilst the *phenylthiocarbamide* is a yellowish oil, which does not solidify at low temperatures; the *nitroso-derivative* is a deep yellow liquid, which boils at $175\text{--}176^\circ$, and *methylpropylamine methylpropyldithiocarbamate* is a viscous, yellowish oil.

Methylisobutylamine is a limpid, colourless liquid of ammoniacal, fish-like odour, and is highly inflammable; it has the sp. gr. = 0.7222 at 18° , and boils at $76\text{--}78^\circ$. It is formed from the *base*, CHPr^2NMe , a colourless liquid, boiling at $65\text{--}70^\circ$, produced by the action of methylamine on isobutaldehyde, and is obtained from it by reduction with sodium and alcohol. The *hydrochloride*, which is but slightly hygroscopic, crystallises in white leaflets, and melts at $177\text{--}179^\circ$; the *platinochloride* forms deep red prisms, and melts at 192° . The *carbamide* and *phenylcarbamide* melt at $145\text{--}146^\circ$, and $124\text{--}125^\circ$ respectively, and the *phenylthiocarbamide* crystallises from dilute alcohol in white leaflets, and melts at 92° ; the *nitroso-derivative* boils at $186\text{--}188^\circ$, and *methylisobutylamine methylisobutyldithiocarbamate* crystallises in yellow needles, and melts at 52° . The

benzoyl derivative is a colourless oil of aromatic odour, and boils at 290—292°.

Methylisoamylamine is obtained when isovaleraldehyde is employed instead of isobutaldehyde, and is a colourless, limpid liquid, of highly disagreeable, fish-like odour; it has the sp. gr. = 0.7390 at 22°, and boils at 108°. The *hydrochloride* is not hygroscopic, and melts at 177°; the *platinochloride* crystallises in small, yellow needles, and melts at 196°. The *carbamide* and *phenylcarbamide* melt at 122° and 100° respectively, and the *phenylthiocarbamide* at 43°; the *nitroso-derivative* and *benzoyl derivative* boil at 206° and 296—298° respectively, and *methylisoamylamine methylisoamylthiocarbamate* is a yellowish oil.

The *carbamide* of methylisobutylhydrazine, $\text{NH}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{NMe} \cdot \text{C}_4\text{H}_9$, crystallises in white needles, and melts at 99°. M. O. F.

Electrolysis of Acids of the Acetic Series. By JULES HAMONET (*Compt. rend.*, 1896, **123**, 252—254).—The author finds that, contrary to the statements of Kolbe, in many cases when solutions of acids of the acetic series are electrolysed, scarcely any paraffin is produced, but an olefine is the chief product; and also that an alcohol containing C_n is always formed from an acid containing C_{n+1} . The alcohol seems to result from the hydrolysis of the ether that is well known to be formed, or else from the hydration of the olefine. More condensed products are also always produced in small quantity.

With a current of 5 ampères and 6 volts, potassium butyrate yields propylene, a small quantity of isopropyl alcohol, and a still smaller quantity of isopropyl butyrate; neither hexane nor primary propyl alcohol is formed. Potassium isobutyrate, under the same conditions, yields practically the same products. C. H. B.

Development of Rancidity in Fats. By EDUARD SPAETH (*Zeits. anal. Chem.*, 1896, **35**, 471—493).—Although the most divergent views have been put forward with regard to the cause of the development of rancidity in fats, the more recent researches (those of Duclaux, Ritsert, and von Klecki) have demonstrated conclusively that the process is one of oxidation by the oxygen of the air, and that it is favoured by access of light. By the examination of 14 samples of lard which had been kept for three years in loosely corked flasks, the author has endeavoured to elucidate more in detail the changes which have taken place.

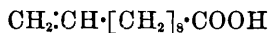
Concurrently with the development of free acidity, a marked decrease in the capacity for absorbing iodine takes place. Of the free acids produced, the greater part is insoluble in water, but soluble acids, and others which are volatile (by the Reichert-Meissl process) are also produced. Amongst the soluble acids, formic, acetic, and butyric have been detected with certainty. The average molecular weight of the total fatty acids is lowered. The iodine absorption of the fluid fatty acids (Muter and De Koningh's number) falls to about the same extent as that of the fat itself. The free acids of the rancid fat exhibit the same iodine absorption

as the neutral fat. The refractive index of the fat shows an increase; that of the fatty acids does not. An increase in the acetyl-number (Abstr., 1887, 620) of the fat occurs, and generally a slight rise in the melting point takes place.

The conclusions drawn from these facts are as follows. In the first place, the glycerides, both of the saturated and unsaturated fatty acids, split up into glycerol and the free acids. The unsaturated acids (mainly oleic) then further decompose into acids containing fewer carbon atoms, together with (as shown by von Raumer) aldehydes; hydroxy-fatty acids are at the same time formed. Simultaneously, the unsaturated acids undergo polymerisation, but the polymerides split up again into the simpler acids when saponified.

M. J. S.

Dehydroundecylenic acid, $\text{CH}_3\text{C}\cdot[\text{CH}_2]_8\text{COOH}$. By FRIEDRICH KRAFFT (*Ber.*, 1896, 29, 2232—2240).—Experiments are described tending to prove the correctness of the formula



for undecylenic acid.

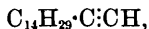
On treating undecylenic acid dibromide with alcoholic potash at high temperatures, a rearrangement of the atoms evidently ensues, with the formation of undecolic acid, $\text{CMe}\cdot\text{C}\cdot[\text{CH}_2]_7\text{COOH}$, the correctness of the formula for which is placed beyond doubt from its ready conversion into azelaic acid, $\text{COOH}\cdot[\text{CH}_2]_7\text{COOH}$, on oxidation. The rearrangement is similar to that which occurs in the production of hexadecylidene from tetradecylacetylene by the same method.

That not only the temperature, but also the alcoholic potash, plays an important part in this rearrangement, is shown by the treatment of bromundecylenic acid in alcoholic solution with potassium carbonate, and the subsequent dry distillation of the potassium salt thus formed; by these means, a compound quite different from undecolic acid, although isomeric with it, is produced. This new acid, for which the name *dehydro-undecylenic acid* is proposed, melts at $42.5\text{--}43^\circ$, and yields sebacic acid on oxidation, which is readily distinguished from the azelaic acid produced on the oxidation of undecolic acid. It appears then, that under these circumstances, undecylenic acid has been converted, without rearrangement, into dehydro-undecylenic acid, $\text{CH}_3\text{C}\cdot[\text{CH}_2]_8\text{COOH}$.

By heating dehydro-undecylenic acid with a very concentrated aqueous solution of potash at 180° , it is completely converted into undecolic acid (m. p. 58°).

The close relation of dehydro-undecylenic acid to undecylenic acid is further shown from its direct production from the dibromide of undecylenic acid on treatment with alcoholic potash at low temperatures.

In the same way, monobromhexadecylene, when treated with alcoholic potash at low temperatures, yields tetradecylacetylene,



whilst, as has been previously shown, at higher temperatures, re-

arrangement ensues, with the formation of methyltridecylacetylene, $C_{13}H_{27}C:CMc$.

Ethylic dehydro-undecylenate, $CH:C[CH_2]_8COOEt$, is formed on heating the acid with dry potassium carbonate, and warming the potassium salt thus formed with ethylic iodide; it is a colourless oil boiling at 145° (15 mm.), and behaves as a true acetylene derivative, forming a silver compound crystallising in glistening plates, from which, on treatment with hydrochloric acid, the ethylic salt is regenerated.

In the production of dehydro-undecylenic acid from bromundecylenic acid, it was noticed that a comparatively large quantity of the bromo-acid remained unchanged; this was separated and again subjected to treatment with alcoholic potash, remaining, however, unaltered. Only after prolonged heating in an autoclave at 180° with alcoholic potash was undecolic acid produced, without the intermediate formation of dehydro-undecylenic acid. The author explains this fact by supposing that two isomeric modifications of bromundecylenic acid exist, the *trans*-configuration $\begin{matrix} Br \\ H \end{matrix} > C:C < \begin{matrix} C_9H_{17}O_2 \\ H \end{matrix}$ being comparatively stable towards alcoholic potash. A similar instance was noted in the case of hexadecylene bromide. J. F. T.

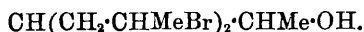
The Combination of Hydrogen Bromide with Diallylacetic acid and Diallylacetone. By ERWIN OBERREIT (*Ber.*, 1896, 29, 1998—2005).—When hydrogen bromide is passed into an alcoholic solution of ethylic diallylacetate, the crude product contains ethylic dibromodipropylacetate, together with the bromopropylvalerolactone,

$CHMe < \begin{matrix} CH_2-CH-CH_2 \\ O-CO \end{matrix} CHMeBr$, previously obtained by Hjelt and

Fittig (*Annalen*, 1882, 216, 73) by the action of hydrogen bromide on the free acid. This is shown by the fact that when the crude product is treated with alcohol and zinc dust, it yields dipropylacetic acid and α -propylvalerolactone, $CHMe < \begin{matrix} CH_2-CHPr \\ O-CO \end{matrix}$. The latter is an

oil which boils at $228-231^\circ$, has a characteristic odour, and is almost insoluble in water. The *silver salt* of the corresponding acid crystallises in small needles. The *methylic salt* is a thick oil, and decomposes into the lactone and methylic alcohol when heated or simply kept over sulphuric acid.

When diallylacetone is treated in ethereal solution with sodium, it is converted into asymmetric *diallylisopropyl alcohol*, which is an oil boiling at $184-185^\circ$. This alcohol readily unites with hydrogen bromide, forming dibromodipropylisopropyl alcohol,



When treated with alcohol and zinc dust, this product is converted into a substance boiling at $158-159^\circ$, which appears to have the formula $C_8H_{16}O_4$, but the constitution of which is not yet understood, and a *hydrocarbon*, C_9H_{20} , which boils at $138-139^\circ$; it has the sp. gr. 0.7407, and the molecular refraction 43.4. A. H.

$\alpha\beta$ -Dimethylglutaric acid. By CLEMENS MONTEMARTINI (*Ber.*, 1896, 29, 2058—2061).—The author has shown (*Real. Accad. Lincei*, 4, 110) that by the interaction of ethylic sodiomethylmalonate and alkylic salts of γ -chlorobutyric acid, two acids are obtained, one, a solid, identical with α -methyladipic acid, and the other, a liquid, of uncertain structure. The two foregoing acids are not interconvertible, and are therefore not stereoisomeric; it appeared probable, therefore, that the production of the liquid acid was due to the initial formation of a crotonic acid whose condensation with ethylic sodiomethylmalonate would result in the production of $\alpha\beta$ -dimethylglutaric acid. The latter substance was therefore synthesised in the following manner.

Twenty grams of ethylic methyllevulinate were mixed with 8.3 grams of potassium cyanide, and the whole gradually added to 24 grams of ice-cold sulphuric acid. After remaining 24 hours, the liquid was diluted, and the precipitated oil separated and hydrolysed with alcohol and hydrogen chloride. The excess of alcohol was then distilled off, and the product shaken with water and extracted with ether, when 14 grams of an oil, consisting of ethylic α -hydroxy- $\alpha\beta$ -dimethylglutarate, was obtained. This was at once heated with hydriodic acid during six hours, and the whole once more extracted with ether. In this way an oily mixture of acids was obtained, from which crystals of glutaric acids separated; the liquid portion was distilled under reduced pressure, when it passed over at about 200° , undergoing partial conversion into the anhydride. The pure acid finally obtained gave numbers agreeing with those required for a dimethylglutaric acid, and consisted of a non-crystallisable liquid. It yielded a crystalline calcium salt, from which the silver salt was obtained as a grey-white, crystalline substance, somewhat soluble in boiling water. When treated with acetic chloride, it gives the anhydride; the anilic acid and anilide are readily obtained in the form of oils.

The synthetical $\alpha\beta$ -dimethylglutaric acid is identical in every respect with the liquid acid obtained from alkylic γ -chlorobutyrate and ethylic sodiomethylmalonate. A. L.

Lyxonic acid. By EMIL FISCHER and OTTO BROMBERG (*Ber.*, 1896, 29, 2068; compare this vol., i, 348).—The authors confirm Bertrand's statement (*Bull. Soc. Chim.*, 1896, [3], 15, 592) that the phenylhydrazide of lyxonic acid crystallises with $2H_2O$.

J. J. S.

Derivatives of Formylcarbamide. By TH. VON GORSKI (*Ber.*, 1896, 29, 2046—2050).—Formylcarbamide melts at 168 — 169° , and not, as has been stated, at 159° ; it crystallises from acetic acid and alcohol, and, when its aqueous solution is evaporated over sulphuric acid, decomposes into formic acid and carbamide.

Formylmalonuric acid, $CHO \cdot NH \cdot CO \cdot NH \cdot CO \cdot CH_2 \cdot COOH$, is formed when formylcarbamide and malonic acid, in molecular proportion, are dissolved in glacial acetic acid and gently warmed on the water bath. The whole sets to a crystalline pulp, which, after filtration and extraction with ether, is crystallised from hot water or acetic

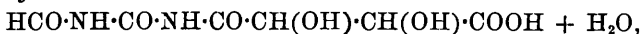
acid. It forms a white, silvery mass of crystals, and melts at $189-199^{\circ}$, the fusion being accompanied by frothing; it is sparingly soluble in hot water, acetic acid, and alcohol. When it is boiled with alkalis, and the resulting solution acidified and distilled, formic acid is found in the distillate. The *barium* salt, $(C_5H_5N_2O_5)_2Ba$, is precipitated, on the addition of barium chloride to an ammoniacal solution of the acid. The *silver* salt, $C_5H_5N_2O_5Ag$, is obtained as a white, crystalline precipitate, rapidly affected by light; it dissolves somewhat readily in water, but is only sparingly soluble in alcohol.

Formylsuccinuric acid, $CHO \cdot NH \cdot CO \cdot NH \cdot CO \cdot C_2H_4 \cdot COOH$, melts at $136-138^{\circ}$, dissolves sparingly in water and alcohol when cold, but readily when hot. The *silver* salt, $C_6H_7N_2O_5Ag$, is crystalline, and dissolves very readily in water. The *methylic* salt crystallises in white needles, and melts at $63-65^{\circ}$.

Formyloxaluric acid, $CHO \cdot NH \cdot CO \cdot NH \cdot CO \cdot COOH + 3H_2O$, is readily soluble in cold water, but with difficulty in boiling alcohol; from either solvent it separates in beautiful needles, and melts and gives off gases at 175° . The *barium* salt, $C_4H_2N_2O_5Ba$, is somewhat soluble in water, and, as it contains two equivalent proportions of barium, it is probable that an imidic hydrogen is here replaced. The *silver* salt, $C_4H_2N_2O_5Ag$, is crystalline and white. Formyloxaluric acid, when dried at $115-120^{\circ}$, slowly evolves carbonic oxide, and yields cyanuric acid.

On attempting to prepare formylmaluric acid from malic acid, in the above manner, the *ammonium* salt, with H_2O , is produced; this crystallises from water in shining, transparent leaflets melting at $128-130^{\circ}$; its aqueous solution, on admixture with silver nitrate, yields a precipitate of the *silver* salt, $C_6H_7N_2O_6Ag$. The latter is readily decomposed by hydrogen sulphide, with production of free *formylmaluric acid*, $HCO \cdot NH \cdot CO \cdot NH \cdot CH(OH) \cdot CH_2 \cdot COOH$, a thick oil excessively soluble in water.

Formylracemuric acid,



crystallises in elongated tables; its water of crystallisation is, in part, retained at 120° , but, at 256° , the substance melts and decomposes; it is soluble in cold water and alcohol, but insoluble in ether. A. L.

Alloxantin as a Decomposition Product of Convicin from Sow-beans and Vetches. By C. HEINRICH L. RITTHAUSEN (*Ber.*, 1896, 29, 2106—2107; compare this vol., i, 416).—By further tests, the author has fully established the identity of alloxantin from convicin with alloxantin from uric acid. M. O. F.

Formation of Active β -Asparagine. By ARNALDO PIUTTI (*Ber.*, 1896, 29, 2069—2071).—Alcoholic ammonia reacts with levorotatory bromosuccinamic acid at the ordinary temperature to form ammonium fumarate, which decomposes at $210-212^{\circ}$. When, however, the bromosuccinamic acid is heated with excess of alcoholic ammonia at 160° , a small quantity of aspartamide (*Abstr.*, 1887, 1031) is formed. Aspartamide, when heated with aqueous ammonia at $100-105^{\circ}$, yields an inactive asparagine which, according to the

crystallographic researches of La Valle, consists of a mixture of equal parts of the two optically active asparagines. The method is not to be recommended, either for simplicity or good yield.

By the action of a concentrated alcoholic solution of ammonia on maleic anhydride at 105–110°, a yellow substance is obtained; this, when dissolved in water and treated with Peligot's copper oxide, gradually yields small crystals of an insoluble copper salt.

This copper salt, when treated with hydrogen sulphide, yields a mixture of the two natural asparagines. About a fourth of the anhydride is converted by this method into β -asparagine, and the author recommends the method as a convenient one for the preparation of *d*-asparagine. J. J. S.

Vinyltrimethylene. By GABRIEL GUSTAVSON (*J. pr. Chem.*, 1896, [2], 54, 97–104).—*Vinyltrimethylene*, $\begin{array}{c} \text{CH}_2 \\ | \\ \text{CH}_2 \end{array} > \text{CH} \cdot \text{CH} \cdot \text{CH}_2$, is a pro-

duct of the action of zinc dust and alcohol on penta-erythritol tetrabromhydrin (Abstr., 1892, 127). Equal weights of zinc dust and the tetrabromhydrin are mixed in a flask and covered with aqueous alcohol (40–60 per cent.); the flask is provided with a vertical tube to condense as much of the alcohol as possible, and the other end of the tube opens into a receiver cooled by ice-cold water. The flask is warmed on the water bath until the action begins, and again when it has abated, so as to distil over the hydrocarbon. The distillate is washed with water and dried by calcium chloride; the yield is 70–75 per cent. of the weight of the penta-erythritol.

Vinyltrimethylene boils at 40°; its specific gravity is 0.7237 at 18°/4°, 0.7431 at 0°/4°, and 0.7229 at 20°/0°; its odour resembles that of allyl compounds, but is somewhat sweeter. It combines with two atoms of bromine, the *bromide*, $\text{C}_3\text{H}_5\text{CHBr} \cdot \text{CH}_2\text{Br}$, boiling at 185–190°, at which temperature slight decomposition occurs.

Oxidation of the hydrocarbon with permanganate yields the *glycol*, $\text{C}_5\text{H}_8(\text{OH})_2$, even when sufficient available oxygen is present to form the compound $\text{C}_5\text{H}_8(\text{OH})_4$. The glycol is a syrupy liquid of sweet taste; it boils at 206–207°, does not solidify at –20°, and has a sp. gr. = 1.094 at 0°/0° and 1.059 at 20°/0°; it is readily brominated to the dibromide, and oxidised by nitric acid to $\alpha\gamma$ -hydroxyglutaric acid.

The refractive index of the hydrocarbon, calculated according to the formula $\frac{M}{d} \left(\frac{n^2 - 1}{n^2 + 2} \right)$, is, for sodium light, $M = 23.40$ at 18.5°, and 23.39 at 20°. The value, calculated according to Brühl's method, is 22.6. A. G. B.

Ethylidenetrimethylene. By GABRIEL GUSTAVSON (*J. pr. Chem.*, 1896, [2], 54, 104–107).—*Ethylidenetrimethylene*, $\begin{array}{c} \text{CH}_2 \\ | \\ \text{CH}_2 \end{array} > \text{C} \cdot \text{CHMe}$, is prepared from the product of the action of hydriodic acid on vinyltrimethylene (preceding abstract). This *iodide*, $\begin{array}{c} \text{CH}_2 \\ | \\ \text{CH}_2 \end{array} > \text{CH} \cdot \text{CHMeI}$, is obtained by adding rather less than the calculated quantity of

vinyltrimethylene to a saturated (at 0°) solution of hydrogen iodide in glacial acetic acid; after 12 hours, the solution is poured into water, and the separated iodide is washed with sodium hydrogen sulphite solution. The iodide boils at 57° (50 mm.); its sp. gr. = 1.625 at 0°/0°, and 1.598 at 20°/0°. By Meyer and Locher's test, it gives a green colour to the chloroform.

The new hydrocarbon is obtained by heating the iodide in a sealed tube at 100°, with alcoholic potash, for 10 hours, and then adding water to the contents of the tube to separate the hydrocarbon. It boils at 37.5° (750 mm.), and differs in odour from vinyltrimethylene. Its sp. gr. = 0.7235 at 0°/4°, and 0.7052 at 18°/4°; its refraction is $n_D = 23.5$. In chemical behaviour, ethyldidenetrimethylene closely resembles vinyltrimethylene. The *iodide*, obtained by the action of hydrogen iodide on the hydrocarbon, boils at 54° (35 mm.), and is somewhat lighter than the above iodide, sp. gr. = 1.588 at 0°/0°, and 1.559 at 20°/0°; by Meyer and Locher's test it gives no colour to the chloroform. When warmed with water, the iodide yields an alcohol which boils at 114–117°, and is being investigated. A. G. B.

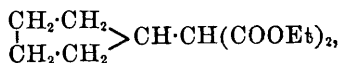
Tetramethylene-1 : 3-dioxalylic acid. By O. KALTWASSER (*Ber.*, 1896, 29, 2273–2281).—Paraformaldehyde reacts with pyruvic acid in presence of sulphuric acid to form *tetramethylene-1 : 3-dioxalylic acid*, $\text{COOH} \cdot \text{C}(\text{OH}) : \text{C} \begin{smallmatrix} \text{CH}_2 \\ \text{CH}_2 \end{smallmatrix} > \text{C} : \text{C}(\text{OH}) \cdot \text{COOH}$, which crystallises in plates, and melts and decomposes at 239.5–240.5°. The aqueous solution of the acid gives a deep reddish-brown coloration with ferric chloride, and reduces ammoniacal silver solution and Fehling's solution. The acid is very readily decomposed by alkalis, with formation of oxalic acid and ethylene.

The *potassium salt* crystallises in matted needles, and the *silver salt* in lustrous plates. The *piperidine salt* also forms plates, and melts at 145–147°. The *phenylhydrazine salt* is deposited from an alcoholic solution of the two constituents in groups of concentrically arranged needles, which melt at 194°.

In acetic acid solution, however, phenylhydrazine yields the *phenylhydrazide* of the acid, which is a yellow, crystalline, sparingly soluble substance, decomposing and melting at 225–227°.

Concentrated sulphuric acid converts the acid into an *anhydride*, $\text{C}_8\text{H}_4\text{O}_4$, which crystallises in prisms, and melts above 300°. Alkalis convert it first into the acid, and then into the decomposition products of the latter. The acid readily combines with 4 atoms of chlorine or bromine. The *chlorine additive product* crystallises in white needles melting and decomposing at 182.5°–183.5°, whilst the *bromine compound* melts and decomposes at 165–170°. The molecular weight of the acid in alcoholic solution corresponds with the formula given above, and its properties show that it has the constitution represented by this, and not by the tautomeric, formula. The paraformaldehyde, therefore, in the formation of this acid reacts as methylene glycol. The acid is accompanied by a second acid melting at 284.5–286.5°, the constitution of which has not yet been determined. A. H.

Pentamethenylmalonic acid and Pentamethenylacetic acid. By AART VERWEY (*Ber.*, 1896, **29**, 1996—1998).—Iodopentamethylene reacts with ethylic sodiomalonate, in presence of toluene, to form *ethylic pentamethenylmalonate* [*cyclopentylmalonate*],



which boils at 137—138° (pressure = 13 mm.). It is very readily hydrolysed by alcoholic potash, and the *potassium salt* is a hygroscopic, crystalline powder. The *free acid* crystallises in slender, white needles, which melt at 162—163°, and are readily soluble in water, alcohol, and ether. It decomposes when heated, forming *pentamethenylacetic* [*cyclopentylacetic*] acid, $\text{C}_5\text{H}_9\cdot\text{CH}_2\cdot\text{COOH}$, which is an oil boiling at 139—140° (pressure = 26 mm.). The *silver salt* crystallises from hot water in slender needles. The *ethylic salt* boils at 191—192°.

A. H.

Influence of Substitution on the Course of some Reactions.

By PAVEL IW. PETRENKO-KRITSCHENKO and E. ARZIBASCHEFF (*Ber.*, 1896, **29**, 2051—2054).—When hexamethylene ketone and benzaldehyde react in presence of sodium ethoxide, a condensation product, *dibenzylidenehexamethylene ketone*, $\text{CH}_2 < \begin{array}{c} \text{CH}_2\cdot\text{C}(\text{CHPh}) \\ \text{CH}_2\cdot\text{C}(\text{CHPh}) \end{array} > \text{CO}$, is obtained; this separates from alcohol, in which it is sparingly soluble, in yellow crystals, and melts at 117°.

Ethylic dimethyl- and diethyl-acetonedicarboxylates do not readily react with aldehydes under normal conditions, benzaldehyde yielding little or no condensation product; acetaldehyde, however, when treated with the above salts in presence of hydrogen chloride, yields some quantity of a substance of high-boiling point, the description of whose properties the authors defer.

That the difference in the behaviour of acetaldehyde and of benzaldehyde under the foregoing conditions is not due to the greater molecular weight of the latter is shown by the ready interaction of isobutylic acetonedicarboxylate (whose molecular weight is equal to that of ethylic diethylacetonedicarboxylate) and benzaldehyde. *Isobutylic acetonedicarboxylate*, prepared by saturating a mixture of the constituents with hydrogen chloride, boils at 220° under 120 mm. pressure; it reacts readily, both with benzaldehyde and with acetaldehyde, yielding, in the latter instance, a thick, oily product, which boils at 218—223° under 60 mm. pressure, and probably has the constitution $\text{O} < \begin{array}{c} \text{CHMe}\cdot\text{CH}(\text{COO}\cdot\text{C}_4\text{H}_9) \\ \text{CHMe}\cdot\text{CH}(\text{COO}\cdot\text{C}_4\text{H}_9) \end{array} > \text{CO}$.

The authors are of opinion that the above facts are to be explained on stereochemical considerations.

A. L.

“Excited” Metals (Metal Couples). Use of Excited Aluminium for Reduction in Neutral Solution. By HANS WISLICENUS (*J. pr. Chem.*, 1896, [2], **54**, 18—65).—The author deems it better to speak of a metal the activity of which is enhanced by

contact with another metal as "excited" (*activirte*), than to adopt the name "metal couple," suggested by Gladstone and Tribe. Some details of the application of aluminium excited by contact with mercury are given, the principles of which have already received notice (*Abstr.*, 1895, i, 437, 634). The best method of preparing aluminium in this condition consists in covering aluminium powder ("aluminiumgries") with a solution of mercuric chloride in absolute alcohol, made by diluting a saturated solution with 10 times its volume of the solvent; after a few seconds, the powder is washed with absolute alcohol and ether. In the event of alcohol being objectionable, ether may be substituted as the solvent for the mercuric chloride.

It is especially for reduction in neutral solutions that excited aluminium is applicable. Its action on an aqueous alcoholic solution of nitrobenzene produces aniline, unless the temperature be kept at 40—50°, when β -phenylhydroxylamine is formed. A better yield (85—90 per cent. of that theoretically possible) of the latter is obtained when an ethereal solution of nitrobenzene is used; cooling is here essential. Orthonitracetophenone reacts with the aluminium more easily than nitrobenzene does; the product appears to be a hydroxylamine derivative, but has not yet been identified.

The conversion of ethylic oxalacetate into ethylic malate by excited aluminium is attended by a much better yield than when sodium amalgam is used. The reduction of ketones by this method avoids the formation of the resinous products which characterise other methods; the behaviour of several ketones under this treatment is described. The discussion between Friedländer, Debus, and Eghis concerning the reduction of ethylic oxalate by sodium amalgam, renders the behaviour of this compound under the new method in neutral solution of especial interest; the chief products prove to be ethylic glycollate and alcohol, a little ethylic desoxalate being formed at the same time. Reduction of the azo-group to the hydrazo-group is particularly smoothly effected by excited aluminium.

A. G. B.

Isomerism of Nitro-compounds. II. By ARTHUR R. HANTZSCH and OTTO W. SCHULTZE (*Ber.*, 1896, 29, 2251—2267; compare this vol., i, 353).—Isophenylnitromethane, when rapidly heated, melts at 84°, and not at 74—76°, as previously stated. The copper salt, $(\text{CHPhNO}\cdot\text{O})_2\text{Cu}$, crystallises in silky needles. When reduced with sodium amalgam, the isonitro-compound yields benzsynalldoxime. All isonitro-compounds and their salts give a sky-blue coloration when they are suspended in ether and treated with a current of hydrogen chloride, or with acetic chloride.

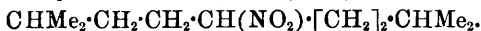
Parabromobenzilylic iodide is obtained by boiling the bromide with potassium iodide solution; it melts at 80—81°, and reacts with silver nitrite to form *parabromophenylnitromethane*. When the sodium salt of this compound is decomposed in aqueous solution by carbonic anhydride, the *normal compound* (*parabromo- α -nitrotoluene*) is precipitated; this crystallises in large, lustrous prisms, melts at 60°, and gives no coloration with ferric chloride. 100 grams of water at 0° dissolve 0.008 gram of it. The isomeric *isobromophenylnitromethane*

is precipitated when hydrochloric acid is added to a solution of the sodium salt. It crystallises in needles, melts at $89-90^{\circ}$, and yields a brownish-red coloration with ferric chloride. 100 grams of water at 0° dissolve 0.056 gram of this substance. When kept, either alone or in solution, it passes into the normal compound. Since the latter does not give the ferric chloride reaction, the passage of the iso-compound into the normal form in solution can be readily followed. Water assists the change in this direction to the greatest extent, chloroform to the least.

That the iso-compound passes into the normal compound in aqueous solution is shown by the fact that the conductivity of an acidified solution of the sodium salt very rapidly decreases for some time, and then becomes constant. This is due to the fact that the free isonitro-compound acts as an acid, and conducts rather better than acetic acid, whilst the normal compound acts as a non-electrolyte. This change of the iso- into the normal-compound in aqueous solution appears to be usually accompanied by the formation of a small amount of nitrous acid. The normal compound cannot itself form salts, but is at once converted by alkalis into the iso-compound, which then dissolves. The normal compounds do not react with phenylic isocyanate, whereas the iso-compounds form diphenylcarbamide. It is found, by the cryoscopic method, that when the iso-compound is dissolved in benzene, its molecular weight is at first twice that of the normal compound, but that it rapidly decreases until it has reached half of its former value. On the other hand, the salts appear to have the monomolecular formulæ.

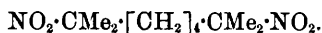
The authors ascribe the formula $R \cdot CH_2 \cdot NO_2$ to the normal compounds, and $R \cdot CH < \begin{smallmatrix} N \cdot OH \\ O \end{smallmatrix}$ to the iso-derivatives. A. H.

Nitration of Saturated Hydrocarbons. II. By MICHAEL I. KONOWALOFF (*Ber.*, 1896, **29**, 2199—2205; compare *Abstr.*, 1894, i, 265, 277, and 1895, i, 633). I. [With NIKITIN].—Diisoamyl, on treatment with dilute nitric acid, yields a tertiary nitro-derivative together with a small quantity of a mixture of two secondary nitro-compounds, namely, $CHMe_2 \cdot CH(NO_2) \cdot [CH_2]_3 \cdot CHMe_2$ and



This mixture, on distillation under a pressure of 25 mm., can be separated into a larger fraction which passes over at $129-132^{\circ}$ and a smaller fraction which boils at $132-135^{\circ}$; the former fraction does not crystallise when placed in a freezing mixture, and has a sp. gr. = 0.9115 at $20^{\circ}/0^{\circ}$. The mixture of secondary nitro-compounds, on reduction, yields a mixture of amines, from which a decylamine, $C_{10}H_{21} \cdot NH_2$ was obtained; boiling at $190-192^{\circ}$, and having a sp. gr. = 0.7934 at $20^{\circ}/0^{\circ}$. Its *hydrochloride*, *nitrate*, and *aurochloride* do not crystallise readily, but the *platinochloride*, which is only sparingly soluble in water, but readily in alcohol, is characteristic. Another product of the reduction of the secondary nitro-compounds is a neutral ketonic substance which gives no crystalline compound with sodium hydrogen sulphite.

A dinitro-derivative, $C_{10}H_{20}(NO_2)_2$, was also obtained by the action of dilute nitric acid on diisoamyl; it melts at $101.5-102^\circ$, is insoluble in water, alkalis, and acids, only sparingly soluble in ether and light petroleum, but readily in benzene, from which it crystallises in long prisms. It sublimes at 100° , is slowly volatilised in a current of steam, and its heat of combustion, calculated on 1 gram-molecule, is 1513614 cal. Since the same compound can be obtained by the further nitration of the previously described tertiary mononitrodiisoamyl it follows that its constitution must be



On reduction, it yields a *diamine* which boils at $223-225^\circ$. This crystallises when cooled in snow, is fairly readily soluble in water, rapidly absorbs carbonic anhydride from the atmosphere, and is volatile with ether vapour. Its *hydrochloride*, *sulphate*, and *platinochloride* are readily soluble in water, the *oxalate* but sparingly.

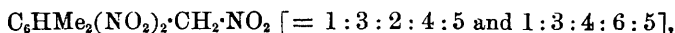
II. [With FR. KIKINA and TSCHITSCHKIN.]—The authors have repeated the experiments of Fittig (*Annalen*, **147**, 2), of Schultz (Abstr., 1884, 904), and of Biedermann and Ledoux (this Journal, 1875, 569), on the nitration of mesitylene, and it is found that in every case, besides the ordinary nitromesitylene mentioned by these authors, an *w*-nitromesitylene is also formed. If Schultz's method is adopted, the two compounds are formed in about equal quantities, the other methods yield far less of the *w*-compound. *w*-Nitromesitylene (1:3:5-xylylnitromethane), $C_6H_3Me_2 \cdot CH_2 \cdot NO_2$, is readily soluble in alkalis, from which it can be precipitated by carbonic anhydride, and it melts at $46-47^\circ$. It dissolves at the ordinary temperature in fuming nitric acid diluted with twice its volume of glacial acetic acid, but remains unaltered even on warming on the water bath. When treated with 5 parts of nitric acid (sp. gr. = 1.47), this mononitro-compound is converted into *w*-orthodinitromesitylene,



It crystallises from benzene in yellowish monoclinic (?) octahedra, melts at $85.5-86^\circ$, is only sparingly soluble in alkali carbonates, but readily in alkali hydroxide solutions, yielding orange-red salts. On oxidation, it yields orthonitromesitylenic acid.

On treating the *w*-nitromesitylene with a large excess of pure nitric acid, a mixture of two trinitromesitylenes was obtained. The one crystallises from alcohol in large plates or in flat needles, and melts at $117-118.5^\circ$. The second could not be obtained in a pure form, but apparently melts between 69° and 73° . They are both readily soluble in alkalis, yielding red salts. The alkali salts of both nitro-compounds give an intensely red precipitate with ferric chloride. Carbonic anhydride and dilute sulphuric acid in the cold precipitate the nitro-compound from solutions of their salts. On oxidation with potassium permanganate, they both yield the corresponding dinitromesitylenic acids, which, however, could not be obtained in a pure state.

These two trinitro-derivatives must have the constitutions



but the author has not determined which belongs to the lower, and which to the higher, melting nitro-compound.

The heat of combustion per gram-molecule of the isomeric mono- and di-nitromesitylenes was determined with the following results.

$C_6H_2Me_3 \cdot NO_2$	1216660 cal.
$C_6H_3Me_2 \cdot CH_2 \cdot NO_2$	1206332 „
$C_6HMe_3(NO_2)_2$	1186710 „
$NO_2 \cdot C_6H_2Me_2 \cdot CH_2 \cdot NO_2$	1165857 „

J. J. S.

Action of Acids on Salts of Nitro-compounds. By MICHAEL I. KONOWALOFF (*Ber.*, 1896, **29**, 2193—2198; compare Nef, this vol., i, 460; Hollemann, this vol., i, 148; W. Wislicenus, this vol., i, 369; Hantzsch and Schultze, this vol., i, 353).—The author has previously (*J. Russ. Chem. Soc.*, 1893, i, 513, and 1894, i, 78) drawn attention to the fact that by the action of strong acids, such as nitric, sulphuric, and acetic, on the salts of nitro-compounds in the cold, colourless solid compounds could be obtained. These compounds are more fully described in the present communication.

A *labile* form of *ω*-nitromesitylene has been obtained by the action of dilute sulphuric acid on a solution of the sodium salt of ordinary *ω*-nitromesitylene (xylynitromethane) cooled by ice. The precipitated nitro-compound must be filtered at once, and well washed with water, as otherwise it is transformed into a yellow oil. Labile *ω*-nitromesitylene crystallises from benzene in needles, it is readily soluble in sodium carbonate solutions, and gives a characteristic ferric chloride reaction in alcoholic, ethereal, or benzene solution. It is readily soluble in the above solvents and also in acetone and ethylic acetate, but is only sparingly soluble in light petroleum.

The crystals are readily converted, even at the ordinary temperature, and still more quickly in bright sunlight, into a yellow oil, in which the author has found small quantities of the labile compound, larger quantities of the stable compound, and finally an aldehyde-like substance, which yields a crystalline compound with sodium hydrogen sulphite. The labile compound is fairly stable in ice-cold water; when slowly heated, the substance begins to melt at 50° and is completely melted at 59°; when, however, the substance is placed in a bath already at 61° it does not melt below 63°. A solution of this compound in an alkali hydroxide or carbonate, when treated with sulphuric acid, yields the labile compound unaltered, carbonic anhydride, however, precipitates the stable *ω*-nitromesitylene.

The freshly prepared sodium salt of diphenylnitromethane also yields a *labile* form of *diphenylnitromethane* when decomposed with dilute sulphuric acid. The crystals are readily soluble in sodium carbonate solution, and give the characteristic reaction with ferric chloride. At the ordinary temperature, the crystals gradually change to a yellowish oil, impurities rendering them even more readily decomposable; the products of decomposition consist of benzophenone, benzophenoneoxime, and the stable nitro-compound. The crystals are, however, stable at low temperatures, and also in ethereal solution.

A *labile phenylisopropylnitromethane* can be obtained in a similar manner, it melts at 54° , and has properties similar to those of labile compound described above.

The sodium salts of secondary nitrononaphthene and of second nitrodisoamyl yield liquid labile compounds, and phenylethyl nitromethane gives a well crystallised labile isomeride. J. J. S

Preparation of Diphenyliodinium Iodide from Iodobenzene. By H. CONRAD C. WILLGERODT (*Ber.*, 1896, **29**, 200 2009; compare this vol., i, 532).—In the formation of diphenyliodinium iodide from iodoxybenzene and potassium iodide, the solution becomes alkaline and iodine is liberated. It appears probable that the following reactions occur. $\text{PhIO}_2 + 2\text{KI} + \text{H}_2\text{O} = \text{PhI} + 2\text{KOH} + \text{I}_2$; $\text{PhIO} + \text{PhIO}_2 + \text{KOH} = \text{Ph}_2\text{I}\cdot\text{OH} + \text{KIO}_2$. The hydroxide then reacts with potassium iodide to produce iodide, which may combine with free iodine to form the periodate, this substance being actually obtained when concentrated solutions are used and only boiled for a short time. Barium hydroxide in presence of potassium iodide, also produces the iodide. Iodobenzene readily dissolves in baryta water, barium iodate being slowly deposited. The filtrate from this only gives a precipitate with potassium iodide after standing for some time. The author is of opinion that iodoxybenzene may be looked on as the anhydride of an iodoniac acid, and that the solutions in alkalis contain the salt of this acid, which, however, soon decompose. The question is being further investigated. A. E

Derivatives of Phenyl Ether. By CARL HÄUSSERMANN, EUGEN BAUER (*Ber.*, 1896, **29**, 2083—2085; compare this vol., i, 532).—2 : 4'-Dinitrophenyl ether is obtained when the product of the action of parachloronitrobenzene on potassium orthonitrophenol is distilled first in a current of steam, and then under diminished pressure. It forms long, white needles, melts at $103\cdot5^{\circ}$, and is readily soluble in boiling alcohol. When reduced with tin and hydrochloric acid it yields the hydrochloride $(\text{NH}_2\cdot\text{C}_6\text{H}_4)_2\text{O}\cdot 2\text{HCl}$, the free base of which melts at $78\text{--}80^{\circ}$.

2 : 2'-Dinitrophenyl ether, obtained from orthochloronitrobenzene and potassium orthonitrophenol, crystallises in white needles, melts at $114\cdot5^{\circ}$.

Para-paramitrophenoxybenzoic acid, $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{COOH}$, is obtained by adding dipotassium parahydroxybenzoate to an excess of parachloronitrobenzene at 160° ; the temperature of the mixture then gradually raised, and kept at 235° for six hours. The acid crystallises in small, colourless prisms, melts at $236\text{--}237^{\circ}$, is soluble in water, and only sparingly soluble in hot alcohol, ether, benzene. The barium salt crystallises in anhydrous forms, and the methyl salt, which crystallises in felted needles, melts at $108\text{--}109^{\circ}$ and is readily soluble in benzene.

Para-paramidophenoxybenzoic acid, obtained by reducing the nitro compound with tin and hydrochloric acid, crystallises in yellow plates, melts at $193\text{--}194^{\circ}$, and is very sparingly soluble in water.

but more readily in alcohol and in chloroform. It is not decomposed on exposure to the air, and it yields a sparingly soluble *hydrochloride* and *sulphate*. The *barium* salt crystallises in white needles, and the *sodium* salt in silky crystals.

The amido-acid, when diazotised, readily combines with resorcinol, salicylic acid, naphthylaminesulphonic acids, &c., to yield yellow to red dyes.

Parahydroxyphenylic ether, obtained from the corresponding amido-ether, crystallises in fine, colourless, felted needles, melts at 84–85°, and is readily soluble in most organic solvents. Its alkaline solution yields a reddish-brown dye with diazobenzene chloride.

J. J. S.

Duroquinone and the Action of Amido-bases on Quinones.

By LEOPOLD RÜGHEIMER and M. HANKEL (*Ber.*, 1896, **29**, 2171–2175; compare this vol., i, 61).—The author has obtained diamidodurene by reducing the dinitro-derivative with stannous chloride in the presence of alcohol (compare Cain, *Abstr.*, 1895, i, 345); when oxidised with ferric chloride at the ordinary temperature, it yields duroquinone.

The quinone, when heated at 220° for six hours with an excess of aniline, yields duroquinol, but no nitrogenous product could be obtained in a state of purity. That some such product must be formed, in accordance with the views previously expressed (*Annalen*, **287**, 54), follows from the fact, that, however large the excess of aniline used may be, only 50 per cent. of the quinone is converted into the corresponding quinol.

Duroquinoldiacetate, $C_6Me_4(OAc)_2$, obtained by heating the quinol with acetic anhydride, crystallises in fine, colourless needles, and melts at 202–203°. The *dipropionate* melts at 138.5–139.5°.

J. J. S.

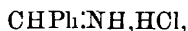
Action of Ammonia and Amines on Bisulphides.

By MAX BUSCH and ALFRED STERN (*Ber.*, 1896, **29**, 2148–2151).—Whilst phenylic and benzylic bisulphides resist the action of alcoholic ammonia or aniline at temperatures approaching 250°, benzoic bisulphide, under the influence of cold alcoholic ammonia gives rise to ammonium thio-benzoate, sulphur, and benzamide; the action of alcoholic aniline converts it into benzanilide, with liberation of hydrogen sulphide and sulphur.

The *bisulphide* of phenylthiocarbazine acid, $S_2(CS \cdot NH \cdot NPh)$ is obtained by the action of an alcoholic solution of iodine on potassium phenylthiocarbazinate, forming a yellow powder, which dissolves with great difficulty in ordinary solvents; alcoholic ammonia converts it in phenylthiosemicarbazide, ammonium phenylthiocarbazinate and sulphur being also produced.

M. O. F.

Benzylideneimide. By MAX BUSCH (*Ber.*, 1896, **29**, 2143–2148; compare this vol., i, 705).—*Benzylideneimide hydrochloride*,



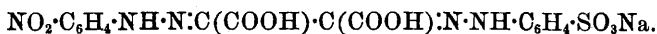
which crystallises in snow-white, lustrous leaflets, is obtained by the

action of alcoholic hydrogen chloride on phenyldithiobiazolone benzyldenesulphime; it is, however, more conveniently prepared by leading dry hydrogen chloride over a continuously agitated solution of hydrobenzamide in benzene to which absolute alcohol (2 mols.) has been added, until absorption ceases, the temperature of the liquid being maintained meanwhile at 5°. The salt melts at 181°, yields ammonium chloride and benzaldehyde on treatment with water, and ammonium chloride and benzylidene diethyl ether under the influence of alcohol; it crystallises from glacial acetic acid in silvery leaflets. On treating benzyldeneimide hydrochloride with alkalis, in order to obtain the free base, ammonia is liberated and hydrobenzamide is produced; ammonia and pyridine produce the same effect, whilst primary amines and hydrazines give rise to benzylidene derivatives and hydrazones respectively.

Benzyldeneimide sulphate crystallises in silvery leaflets, becoming reddish if kept, and melts at 144°; in properties and behaviour towards various agents, it closely resembles the hydrochloride.

M. O. F.

Action of Diazo-compounds on Tartrazin. By ROBERT GNEHM and LOUIS BENDA (*Ber.*, 1896, **29**, 2017—2019).—When a solution of paranitrodiazobenzene chloride is added to an alkaline solution of tartrazin, nitrogen is evolved, and a substance is formed which crystallises in yellow needles, and decomposes when strongly heated leaving a voluminous residue. It dyes wool, in an acid bath, a fine orange shade, very fast to light. This substance probably has the constitution



It can also be obtained from dihydroxytartaric acid, paranitrophenylhydrazine and paraphenylhydrazinesulphonic acid. The nitrogen which is evolved is a secondary product, and arises from the decomposition of the paradiazobenzenesulphonic acid which is formed in the reaction.

A. H.

Diazomethanedisulphonic acid. By HANS VON PECHMANN (*Ber.*, 1896, **29**, 2161—2169; compare this vol., i, 14).—*Potassium azine-methanedisulphonate*, $\text{C}(\text{SO}_3\text{K})_2\cdot\text{N}\cdot\text{N}:\text{C}(\text{SO}_3\text{K})_2$, is obtained by dehydrating powdered dipotassium diazomethanedisulphonate (*loc. cit.*) in an atmosphere of hydrogen at 100°, and heating it in xylene for 10—12 hours at 120—130°; it crystallises from water in rosettes of white prisms, and contains $2\text{H}_2\text{O}$. The action of boiling acids on the substance liberates sulphurous anhydride, and gives rise to the production of hydrazine, whilst a solution of barium chloride yields a precipitate which dissolves in excess of the agent, lustrous leaflets, which do not redissolve when heated, separating from the liquid obtained in this way.

Ethylglyoxylylate phenylhydrazone, $\text{COOEt}\cdot\text{CH}\cdot\text{N}\cdot\text{NHPh}$, is produced when a slightly acid solution of diazobenzeneacetate is added to a solution of potassium ethyl sulphohydrazimethylenecarboxylate (*Abstr.*, 1895, i, 642) at 0°; it crystallises from dilute alcohol in

colourless, rhombic leaflets, and melts at 130—131°. The solution in concentrated sulphuric acid is yellow, and develops a reddish-violet coloration with ferric chloride or potassium dichromate; alcoholic soda acts on it hydrolytically, producing the phenylhydrazone of glyoxylic acid.

Ethyllic formazylformate, $\text{NH}_2\cdot\text{N}\cdot\text{C}(\text{N}_2\text{Ph})\cdot\text{COOEt}$, is obtained by the action of an alkaline solution of diazobenzene (2 mols.) on potassium ethylic sulphohydrazimethylenecarboxylate at 0°; it crystallises from alcohol in leaflets, and melts at 117°. Hydrolysis converts it into formazylformic acid (m. p. 162°).

Potassium phenylhydrazonemethanedisulphonate, $\text{C}(\text{SO}_3\text{K})_2\cdot\text{N}\cdot\text{NHPH}$, is produced when a concentrated solution of diazobenzene acetate ($1\frac{1}{2}$ mol.) is added to the additive sulphite compound of dipotassium diazomethanedisulphonate dissolved in 8 parts of water; after 12 hours, inorganic salts having been removed, and sulphuric acid exactly precipitated with barium acetate, the solution is concentrated. The dipotassium salt crystallises from alcohol or water in flat, lustrous needles; the solution in concentrated sulphuric acid develops a violet coloration with ferric chloride or potassium chromate. Hot acids resolve it into sulphurous anhydride and phenylhydrazine, and sulphurous acid converts it into a compound which is volatile in steam, crystallises in slender needles melting at 88—90°, and is free from sulphur.

Potassium diazobenzenephenylhydrazonemethanedisulphonate,



is obtained from the foregoing salt and diazobenzene; it crystallises in slender, orange-yellow needles which darken on exposure to light, and explodes at 180°. Concentrated sulphuric acid dissolves it with a violet coloration, and mercuric nitrate produces a purple precipitate; alkaline reducing agents develop an intense red coloration, which is fugitive. A solution of the diazoamido-salt is decolorised by cold, dilute acids, alcohol precipitating the original hydrazone; if the liquid is treated with alkali, however, the diazoamido-salt is precipitated. After a short interval, a neutral or alkaline aqueous solution deposits slender needles which melt at 187°, and the liquid contains dipotassium phenylhydrazonemethanedisulphonate and potassium benzenediazosulphonate.

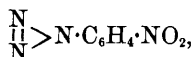
Formazylsulphonic acid, $\text{NHPH}\cdot\text{N}\cdot\text{C}(\text{N}_2\text{Ph})\cdot\text{SO}_3\text{H}$, is obtained by suspending finely divided potassium diazobenzenephenylhydrazonemethanedisulphonate in 10 parts of alcohol, and adding alcoholic hydrochloric acid to the cooled solution. It crystallises from ethylic acetate in violet leaflets having a blue reflex, and sinters at 192°; the solution in concentrated sulphuric acid is blue, and becomes violet on the addition of nitric acid. Boiling dilute acids give rise to sulphurous anhydride and phenylhydrazine, and reducing agents convert it into potassium phenylhydrazonemethanedisulphonate, along with aniline and phenylhydrazine. The *potassium* salt crystallises from much boiling alcohol, and forms red, lustrous needles.

Potassium parabromodiazobenzenephenylhydrazonemethanedisulphonate, $\text{C}(\text{SO}_3\text{K})_2\cdot\text{N}\cdot\text{NPh}\cdot\text{N}\cdot\text{N}\cdot\text{C}_6\text{H}_4\text{Br}$, is prepared from dipotassium

phenylhydrazonemethanedisulphonate and parabromodiazobenzene in alkaline solution; it forms sparingly soluble, orange-yellow needles.

Parabromoformazylsulphonic acid, $\text{NHPh}\cdot\text{N}:\text{C}(\text{N}_2\cdot\text{C}_6\text{H}_4\text{Br})\cdot\text{SO}_3\text{H}$, is produced when the foregoing substance is treated with alcoholic hydrochloric acid; it crystallises from ethylic acetate in violet scales, and sinters at 196° .

Benzoylhydrazonepyruvic acid, $\text{NHBz}\cdot\text{N}:\text{CMe}\cdot\text{COOH}$, is obtained by the action of dilute pyruvic acid on a hot, aqueous solution of benzoylhydrazine, and crystallises from boiling water or dilute alcohol in colourless needles which melt at 112° ; it contains $1\text{H}_2\text{O}$, becoming anhydrous at $110\text{--}115^\circ$, and in this condition melts at 155° . Pyruvic acid is eliminated from the substance under the influence of diazobenzene or the additive sulphite compounds of aliphatic diazo-compounds. Paranitrodiazobenzene has the same effect, converting it into a substance which is probably *paranitrodiazobenzenebenzoylhydrazine*, $\text{NHBz}\cdot\text{NH}\cdot\text{N}:\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$; this forms a lemon-yellow precipitate, and cannot be recrystallised, as boiling water or alcohol converts it into benzamide and *paranitrodiazobenzeneimide*,



which crystallises from petroleum in yellowish leaflets, and melts at $71\text{--}72^\circ$. The latter substance is readily formed by the action of nitrodiazobenzene on hydrazine dissolved in acetic acid, in presence of ammonia; it is volatile in an atmosphere of steam.

M. O. F.

Hydrazides and Azides [Azoimides] of the Phthalic acids.

By THEODOR CURTIUS and ERNST DAVIDIS (*J. pr. Chem.*, 1896, [2], 54, 66—87).—The phthalylhydrazide prepared by the action of hydrazine hydrate on ethylic phthalate and on phthalic chloride is identical with that prepared from phthalic anhydride (Abstr., 1895, i, 354); the crystallography of the compound is given.

Isophthalylhydrazide, $\text{C}_6\text{H}_4(\text{CON}_2\text{H}_3)_2$, is prepared by dissolving ethylic isophthalate (1 mol.) and hydrazine hydrate (1 mol.) in absolute alcohol, and heating on the water bath for four hours; the powder which separates on cooling is crystallised from 80 per cent. alcohol. The hydrazide forms white, silky needles, melting at 220° ; it dissolves easily in warm water, dilute alcohol, and glacial acetic acid, more sparingly in absolute alcohol, but not in ether or benzene. It reduces Fehling's solution, ammoniacal silver nitrate, and platinum chloride in the cold. Prolonged heating with acids decomposes it into isophthalic acid and a hydrazine salt. The *hydrochloride*, $\text{C}_8\text{H}_{10}\text{N}_4\text{O}_2\cdot 2\text{HCl}$, and the *platinosochloride*, $\text{C}_8\text{H}_{10}\text{N}_4\text{O}_2\cdot \text{H}_2\text{PtCl}_4$, are described. The *acetone* [*isopropylidene*] derivative,



crystallises in slender needles, melts at $243\text{--}244^\circ$, and is freely soluble in absolute alcohol and ether. The *benzylidene* derivative, $\text{C}_6\text{H}_4(\text{CO}\cdot\text{NH}\cdot\text{N}:\text{CHPh})_2$, formed by treating the hydrazide with

benzaldehyde, crystallises in colourless needles, melts at 241° , and dissolves sparingly in alcohol and water, but not in ether.

Ethylic isophthallylhydrazidacetoacetate,



prepared by warming isophthallylhydrazide with ethylic acetoacetate, crystallises with difficulty, melts at 145° , and is extraordinarily soluble in alcohol.

Isophthalazoimide, $\text{C}_6\text{H}_4(\text{CON}_3)_2$, prepared by diazotising the hydrazide, crystallises in transparent, anisotropic prisms, melts at 56° , and is freely soluble in ether and acetone; when dry it is somewhat explosive.

When ethylic terephthalate and hydrazine hydrate are heated together on the water bath, only one ethoxy-group is substituted, *ethylic terephthallylhydrazinate*, $\text{NH}_2\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{COOEt}$, being produced in whatever proportions the reacting compounds are mixed. The salt crystallises in slender, white needles, melts at $164\text{--}165^{\circ}$, and dissolves freely in hot water, alcohol, and glacial acetic acid, but not in ether. It is less stable than isophthallylhydrazide, and has similar reducing properties. The *hydrochloride*, $\text{C}_{10}\text{H}_{12}\text{N}_2\text{O}_3\cdot\text{HCl}$, and the *sodium derivative*, $\text{C}_{10}\text{H}_{11}\text{N}_2\text{O}_3\text{Na}$, are described. The *benzylidene derivative* crystallises in slender, colourless needles, and melts at 259° .

Ethylic terephthalylazoimate, $\text{N}_3\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{COOEt}$, obtained by diazotising the hydrazide, crystallises in colourless tables which have an irritating, aromatic odour, melt at the temperature of the hand, and dissolve freely in ether and acetone.

Terephthallylhydrazide, $\text{C}_6\text{H}_4(\text{CON}_2\text{H}_3)_2$, is prepared by heating ethylic or methylic terephthalate (1 mol.) with hydrazine hydrate (2 mols.) and some alcohol for 3 to 4 hours in a tube at $130\text{--}140^{\circ}$. It crystallises in small, felted needles, melts above 300° , and is very sparingly soluble. The *hydrochloride*, $\text{C}_8\text{H}_{10}\text{N}_4\text{O}_2\cdot 2\text{HCl}$, the *benzylidene derivative*, and the *acetone* [*isopropylidene*] derivative (m. p. $261\text{--}262^{\circ}$) are described. *Ethylic terephthallylhydrazidacetoacetate*, $\text{C}_6\text{H}_4(\text{CO}\cdot\text{NH}\cdot\text{N}\cdot\text{CMe}\cdot\text{CH}_2\cdot\text{COOEt})_2$, forms yellowish granular crystals, and melts at 240° .

Formylideneterephthallylhydrazide, $\text{C}_6\text{H}_4(\text{CO}\cdot\text{NH}\cdot\text{N}\cdot\text{CH}_2)_2$, from formaldehyde and the hydrazide, is a grey, insoluble powder; it does not melt at 300° .

Terephthalazoimide, $\text{C}_6\text{H}_4(\text{CON}_3)_2$, prepared like isophthalazoimide, crystallises in colourless tables, melts at 110° , and is freely soluble in ether and acetone. When suspended in dry alcohol and gently warmed until evolution of gas ceases, it is converted into *paraphenylenethylurethane*, $\text{C}_6\text{H}_4(\text{NH}\cdot\text{COOEt})_2$, which crystallises in colourless tables, melts at 195° , and is freely soluble in alcohol, ether, benzene, chloroform, and light petroleum. By heating terephthalazide with water,

paraphenylenecarbamide, $\text{C}_6\text{H}_4\langle\begin{smallmatrix} \text{NH} \\ \text{NH} \end{smallmatrix}\rangle\text{CO}$, is obtained as a reddish, insoluble, crystalline powder. *Metaphenylenethylurethane*, prepared from isophthalazide in the manner indicated for the para-compound, crystallises in small tables, melts at $143\text{--}145^{\circ}$, and shows a solu-

bility similar to that of the para-compound. Metaphenylenecarbamide has been prepared by Michler and Zimmerman (Abstr., 1882, 182). A. G. B.

[**Bromocinnamic Acids: Alloisomerism.**] By ARTHUR MICHAEL (*J. pr. Chem.*, 1896, [2], 54, 107—112).—Comments of a purely controversial character on Erlenmeyer's recent paper (this vol., i, 46), and a reply to the criticisms of Liebermann (this vol., i, 347). A. G. B.

Tautomerism of the Orthoaldehydic Acids. II. By CARL T. LIEBERMANN (*Ber.*, 1896, 29, 2030—2036; compare this vol., i, 232).—The behaviour of orthoaldehydic acids towards bases was further studied with the object of ascertaining in which of their tautomeric modifications they most frequently appeared. Bromo- and nitro-opianic acids behaved towards primary and secondary bases as hydroxyphthalides; the compounds of the former with primary bases, which at first appeared to be more readily changed to the aldehydic acid modification than those of opianic acid itself, are now known to be equally stable. It is better to continue the shaking with soda during a longer period, but 15 minutes suffices to cause the greater portion of the compound to dissolve. Soon after dissolution, however, the excess of soda effects a partial decomposition into base and acid; the liquid is, therefore, quickly filtered and acidified with acetic acid which causes the precipitation of an acid having the normal constitution $\text{COOH} \cdot \text{CH} \cdot \text{CH} \cdot \text{CH} \cdot \text{NR}$. The compounds of the latter type, when damp, dissolve immediately in one per cent. soda solution, but after drying show their original behaviour. Suspecting the existence of compounds intermediate between the above two types, the author has subjected opianic acid β -naphthylamine to careful treatment with soda, &c., but has not succeeded in obtaining evidence of the production of any such substance.

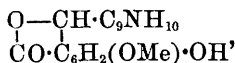
Bromopianic acid β -naphthylamide, $\begin{array}{c} \text{O} - \text{CH} \cdot \text{NH} \cdot \text{C}_{10}\text{H}_7 \\ | \\ \text{CO} \cdot \text{C}_6\text{HBr}(\text{OMe})_2 \end{array}$, melts at 213° , and dissolves in cold soda after continued shaking.

Nitropianic acid β -naphthylamide, $\begin{array}{c} \text{O} - \text{CH} \cdot \text{NH} \cdot \text{C}_{10}\text{H}_7 \\ | \\ \text{CO} \cdot \text{C}_6\text{H}(\text{OMe})_2 \cdot \text{NO}_2 \end{array}$, is very sparingly soluble in alcohol, and melts and decomposes at about 232° . It is insoluble in cold soda, but dissolves, on warming, with production of the sodium salt of nitropian- β -naphthylamic acid.

Methylnoropianic acid melts, not at 140 — 142° , but at 155 — 156° , or, when containing water of crystallisation, at about 100° . *Methylnoropian- β -naphthalidic acid (?)*,

$\text{COOH} \cdot \text{C}_6\text{H}_2(\text{OH})(\text{OMe}) \cdot \text{CH} \cdot \text{N} \cdot \text{C}_{10}\text{H}_7(\beta)$?, or $\begin{array}{c} \text{O} - \text{CH} \cdot \text{NH} \cdot \text{C}_{10}\text{H}_7 \\ | \\ \text{CO} \cdot \text{C}_6\text{H}_2(\text{OMe}) \cdot \text{OH} \end{array}$, is obtained as a beautiful, lemon-yellow crystalline precipitate, on mixing its constituents. It melts and decomposes at about 225° , and dissolves readily in cold soda with production of the sodium salt; the latter, when decomposed by dilute acetic acid, yields

the original substance in yellow, caseous masses. α -Naphthylamine, aniline, and paratoluidine yield similar compounds with methylnoropianic acid; the aniline derivative melts and decomposes at 199°, and the paratoluidine derivative at 211°. The sodium salt of methylnoropianilidic acid seems to contain 1 mol. H_2O , which is lost at 75–105°. *Methylnoropianic acid tetrahydroquinoline*,



separates, on mixing cold alcoholic solutions of its components, in long, white leaflets, being subsequently sparingly soluble in alcohol. When treated with soda, it suddenly coagulates, an effect probably due to the production of a sodium salt. It melts at 231°.

Opianic acid methylketolide, $\begin{array}{c} \text{O}-\text{CH}\cdot\text{C}_9\text{NH}_8 \\ | \\ \text{CO}\cdot\text{C}_6\text{H}_2(\text{OMe})_2 \end{array}$, prepared by the interaction of opianic acid and methylketole, forms silky needles melting at 194°, and is insoluble in soda and strong hydrochloric acid. *Opiananthranilic acid*, $\text{COOH}\cdot\text{C}_6\text{H}_2(\text{OMe})_2\cdot\text{CH}\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{COOH}$, melts at 231°, and dissolves in soda, being reprecipitated unchanged on the addition of acetic acid. Analyses of the barium and calcium salts are in agreement with the above formula.

Tertiary aromatic bases do not yield anhydro-compounds with opianic acid, and, when these mixed solutions in acetone are evaporated, ether separates the base from the sparingly soluble opianic acid. ψ -Tropine, however, combines with opianic acid in acetone solution with production of beautiful, lustrous crystals of ψ -tropine opianate, $\text{C}_8\text{H}_{15}\text{NO}\cdot\text{C}_{10}\text{H}_{10}\text{O}_6$; the latter dissolves readily in water, and is at once decomposed by dilute alkalis or acids, its constituents being regenerated. ψ -Tropine may be separated from tropine by this means. A. L.

Orthophthalaldehydic Acid and Aromatic Bases. By R. GLOGAUER (*Ber.*, 1896, 29, 2036–2039; compare preceding Abstract). —Racine (Abstr., 1887, 951) has shown that orthophthalaldehydic acid combines with aniline with production of a substance, having acid properties, to which he ascribes the formula $\text{COOH}\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{NPh}$; Liebermann, on the other hand, has observed (this vol., i, 232) that its compounds with tetrahydroquinoline, and β -naphthylamine are insoluble in soda, and may be assigned the formulæ $\begin{array}{c} \text{O}-\text{CH}\cdot\text{C}_9\text{NH}_{10} \\ | \\ \text{CO}\cdot\text{C}_6\text{H}_4 \end{array}$

and $\begin{array}{c} \text{O}-\text{CH}\cdot\text{NH}\cdot\text{C}_{10}\text{H}_7 \\ | \\ \text{CO}\cdot\text{C}_6\text{H}_4 \end{array}$, respectively.

In all instances observed by the author, the action may be represented by the scheme:—1 mol. acid + 1 mol. base – 1 mol. water. The compounds with secondary bases are invariably insoluble in cold soda, but are decomposed into acid and base on warming; they, therefore, pertain to the hydroxyphthalide type, $\begin{array}{c} \text{O}-\text{CH}\cdot\text{NR}_2 \\ | \\ \text{CO}\cdot\text{C}_6\text{H}_4 \end{array}$. The compounds with primary bases usually exist in two modifications, and as

the aniline compound dissolves rapidly in soda, the formula assigned to it by Racine is doubtless the correct one.

Phthalaldehydic- α -naphthylamide, $\begin{array}{c} \text{O}-\text{CH}\cdot\text{NH}\cdot\text{C}_{10}\text{H}_7 \\ | \\ \text{CO}\cdot\text{C}_6\text{H}_4 \end{array}$, is soluble with difficulty in aqueous soda, and melts at 155—159°. *Phthalaldehyde- α -naphthylamic acid*, $\text{COOH}\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{N}\cdot\text{C}_{10}\text{H}_7$, prepared by dissolving the preceding substance in dilute soda and precipitating with acetic acid, is readily soluble in soda. *Phthalaldehydic- β -naphthylamide* is dissolved very slowly by soda with production of the readily soluble *phthalaldehyde- β -naphthylamic acid*. *Phthalaldehydic-paratoluidide*, $\begin{array}{c} \text{O}-\text{CH}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\text{Me} \\ | \\ \text{CO}\cdot\text{C}_6\text{H}_4 \end{array}$, melts at 149°, and after continued shaking with soda yields *phthalaldehydeparatoluidic acid*, $\text{COOH}\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{N}\cdot\text{C}_6\text{H}_4\text{Me}$.

Phthalaldehydemethylanilide, $\begin{array}{c} \text{O}-\text{CH}\cdot\text{NMePh} \\ | \\ \text{CO}\cdot\text{C}_6\text{H}_4 \end{array}$, crystallises from alcohol and melts at 150°; it is insoluble in soda but is decomposed by ammonia, phthalaldehydic acid and methylaniline being regenerated. *Phthalaldehydic-tetrahydroisquinolide* melts at 170°, whilst *phthalaldehydic-piperidide*, crystallises from ether in needles melting at 97°.

A. L.

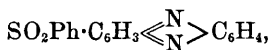
Paratoluenesulphinic acid. By ERNST VON MEYER (*J. pr. Chem.*, 1896, [2], 54, 95—97; compare Piloty, this vol., i, 555).—When ditoluenesulphonylhydroxylamide, $\text{OH}\cdot\text{N}(\text{SO}_2\cdot\text{C}_6\text{H}_5)_2$ (König, Abstr., 1878, 573), is mixed with paratoluenesulphinic acid in glacial acetic acid solution, *tritoluenesulphonamide*, $(\text{C}_6\text{H}_5\text{SO}_2)_3\text{N}$, is obtained; this forms white crystals and melts at 186°. Paratoluenesulphinic acid combines with formaldehyde yielding *paratolylhydroxymethylsulphone*, $\text{C}_6\text{H}_4\cdot\text{SO}_2\cdot\text{CH}_2\cdot\text{OH}$, which melts at 90°. In an ether-alcohol solution of paratoluenesulphinic acid, ammonia precipitates the ammonium salt, which decomposes and melts at 175°; but, in a benzene solution, in the absence of water, an intramolecular decomposition occurs with formation of ammonium paratoluenesulphonate and “paratoluenedisulphoxide,” $\text{C}_6\text{H}_4\text{SO}_2\cdot\text{SC}_6\text{H}_4$.

Aniline paratoluenesulphinate melts at 118°, and at 160° loses water together with some toluene and sulphurous anhydride; the residue yields to alcohol a substance which dissolves with a brilliant blue-violet colour and behaves as an unstable dye.

Well crystallised compounds are obtained from paratoluenesulphinic acid and phenylhydrazine and hydrazine hydrate respectively. The research is proceeding.

A. G. B.

Benzenesulphinic acid as a Reagent. By OSCAR HINSBERG and A. HIMMELSCHNEIN (*Ber.*, 1896, 29, 2019—2023; compare Abstr., 1895, i, 144 and 471).—*Phenazylphenylsulphone*,



prepared by the action of phenazine on benzenesulphinic acid in

presence of hydrochloric acid at 30—40°, crystallises in bright yellow, glistening leaflets, and melts at 244° (uncorr.). It is nearly insoluble in water, but dissolves slightly in alcohol and readily in acetic acid. Its solutions in concentrated sulphuric and hydrochloric acids contain the corresponding salts, but these are decomposed on the addition of water, the sulphone being precipitated. It is not affected by alkalis at 100°, but is reduced to phenylic hydrosulphide by zinc and warm hydrochloric acid. When prepared in the above manner, it is accompanied by the hydrochloride of phenazine and dihydrophenazine, and a small quantity of a substance melting at about 275° and sparingly soluble in acetic acid, probably the disulphone $C_{12}H_6N_2(SO_2Ph)_2$.

Paramidotolylphenylsulphone, $SO_2Ph \cdot C_6H_3Me \cdot NH_2$, is obtained when paramidobenzyl alcohol, or its anhydride, is warmed with dilute hydrochloric acid, and the dark yellow solution of the compound thus obtained (compare Abstr., 1895, i, 299) is mixed with benzenesulphinic acid. It dissolves readily in hot water, forming a colourless solution; the crystals deposited on cooling are colourless, but become yellow on drying, and melt at 176°. It dissolves sparingly in alcohol and glacial acetic acid, forming, in the latter instance, a yellow solution. It gives a colourless, stable hydrochloride, and yields a colourless diazo-compound which reacts with sodium naphthoxide, forming an orange dye. The *acetyl* derivative, $SO_2Ph \cdot C_6H_3Me \cdot NHAc$, is sparingly soluble in water, but dissolves readily in acetic acid and alcohol, and crystallises in colourless needles melting at 201°.

Rosaniline salts do not readily react with benzenesulphinic acid.

A. L.

Hydroxy- and Amido-derivatives of Diphenylsulphone.

By OSCAR HINSBERG and A. HIMMELSCHNEID (Ber., 1896, 29, 2023—2029).

—It is well known that when the ortho- and para-dihydroxy-, diamido- and amido-hydroxy-benzenes, are oxidised with acid reagents, they all, with the exception of quinol, yield coloured substances of complex structure. As it appeared possible that simple derivatives of ortho- and para-quinones were the initial products, the authors have carried out the oxidation of several such di-derivatives of benzene in presence of benzenesulphinic acid which eagerly combines with quinonoid compounds, and, as was expected, instead of highly coloured products, colourless substances were obtained.

Quinol, when oxidised with a cold aqueous solution of potassium dichromate in presence of benzenesulphinic acid, yields 1 : 4-dihydroxyphenylsulphone. Catechol, when treated in a similar manner, gives a bright green chromium compound, from which, by treatment with acetic acid, chromium acetate and 1 : 2-dihydroxyphenylparaphenylsulphone, $SO_2Ph \cdot C_6H_3(OH)_2$, are obtained. The latter, when crystallised from water, contains water of crystallisation which it loses above 110°; the dried substance melts at about 164°, dissolves readily in hot water, alcohol, and acetic acid, and its solutions in alkalis are yellow. Its aqueous solution, when mixed with ferric chloride, gives a bluish-green coloration, changed to red by soda.

Trihydroxyphenylsulphone, $SO_2Ph \cdot C_6H_2(OH)_3$ [(OH)₃ = 1 : 2 : 3], prepared from pyrogallol and benzenesulphinic acid, crystallises from hot water in large, colourless tablets melting at 188°. It dissolves

readily in hot water and alcohol, but is sparingly soluble in ether; ferric chloride produces in its aqueous solution a deep blue colour, changed to red by soda; its alkaline salts give deep yellow solutions. It gives a bluish-black tint to cloth steeped in iron salts.

3:5-Diphenyldisulphoneparaphenylenediamine, $C_6H_2(NH_2)_2(SO_2Ph)_2$, is obtained when paraphenylenediamine is oxidised in acid solution by potassium dichromate in presence of benzenesulphinic acid. It separates from chloroform, on the addition of light petroleum, as a yellow, crystalline precipitate composed of microscopic needles; it is nearly insoluble in water, and sparingly soluble in ether, but dissolves readily in alcohol and acetic acid, and melts at 115° forming a viscid liquid. When treated with strong hydrochloric or sulphuric acid, it yields colourless salts which are prone to oxidation, assuming a violet colour when exposed to the air. When oxidised in acetic acid solution by potassium dichromate, it yields a red base whose salts are violet. The sulphone, when treated with acetic anhydride, yields a colourless *acetyl* derivative, $C_{18}H_{16}N_2S_2O_4$.

When paramidodimethylaniline is oxidised in presence of benzenesulphinic acid, it yields the same diphenyldisulphonedimethylparaphenylenediamine as is obtained by the direct interaction of nitrosodimethylaniline hydrochloride and benzenesulphinic acid (compare Abstr., 1895, i, 144).

Diphenylsulphoneorthamidophenol, $OH \cdot C_6H_2(SO_2Ph)_2 \cdot NH_2$, is obtained by the oxidation of orthamidophenol in presence of benzenesulphinic acid; water precipitates it from its solution in acetic acid as a yellowish, crystalline mass, which melts, after showing signs of sintering, at about 115° , forming a dark liquid; it is sparingly soluble in water, but is readily dissolved by alcohol and acetic acid; its *sodium* salt dissolves in water, yielding a pure yellow solution from which it is reprecipitated by excess of strong soda. The *hydrochloride* of the disulphone is a yellowish-brown substance which is decomposed by water. A. L.

Diorthodiamidodiphenyl. By ERNST TÄUBER (*Ber.*, 1896, 29, 2270—2272).—Diphenyleneorthodihydrazine (Abstr., 1893, i, 588) crystallises in yellowish plates melting at 110° . The *hydrochloride* forms lustrous plates, and the *sulphate* sparingly soluble tablets. At 150° , the hydrazine is converted quantitatively into *diphenyleneazone*, $C_6H_4 \begin{smallmatrix} \diagup N:N \diagdown \end{smallmatrix} C_6H_4$.

The *diacetyl* derivative is only very slightly soluble in the usual solvents, and, when heated, decomposes with formation of acetamide and diphenyleneazone. A. H.

Benzhydrol Ether and the Benzopinacolins. By HEINRICH KLINGER and CARL LONNES (*Ber.*, 1896, 29, 2158—2160).—The compound, $C_{26}H_{20}O$, obtained on melting benzopinacone, was regarded by Thorner and Zincke as identical with benzhydrol ether, which, according to Linnemann, has the formula $C_{26}H_{22}O$ (*Annalen*, 1865, 133, 6). The authors have, therefore, prepared benzhydrol ether by three different methods—heating benzhydrol at its boiling point, heating it

with benzylic acid, and heating it with dilute sulphuric acid at 180° ; in each case the product melts at 109° , and has the formula $C_{26}H_{22}O$. The substance does not yield β -benzopinacolin under the influence of hot acetic chloride, and, as the compound described by Thörner and Zincke undergoes the change in question, the two substances can no longer be regarded as identical.

Although Delacre has ascribed to α -benzopinacolin the bimolecular formula, $C_{52}H_{40}O_2$ (*Bull. Acad. Roy. Belg.*, [3], **21**, 541), an ebullioscopic determination of the molecular weight in acetone establishes the formula $C_{26}H_{20}O$. The compound, obtained by reducing α -benzopinacolin with sodium and amylic alcohol, and represented by Delacre as having the composition $C_{52}H_{42}O$, melts at 210° , and has all the properties of tetraphenylethane.

β -Benzopinacolin also has the formula $C_{26}H_{20}O$, and the two isomerides must be, therefore, represented respectively by the expres-

sions $\begin{array}{c} \text{CPh}_2 \\ | \\ \text{CPh}_2 \end{array} > \text{O}$ and $\text{CPh}_3 \cdot \text{COPh}$.

M. O. F.

Two Isomeric Bromodiphenacyls. By CARL PAAL and KARL DEMELER (*Ber.*, 1896, **29**, 2092—2097).—During an attempt to produce ethylic diphenacylacetate in more remunerative quantity, a mixture of two compounds, having the formula $C_{16}H_{13}BrO_2$, has been obtained; both substances yield diphenacyl on reduction, and one modification is transformed into the isomeride when the alcoholic solution is boiled. The compounds are, therefore, isomeric forms of bromodiphenacyl, a substance which the authors, consequently, regard as capable of existing in both its ketonic and enolic forms (compare Claisen, this vol., i, 557); the possibility of stereoisomerism, however, also presents itself.

Bromodiphenacyl, $C_{16}H_{13}BrO_2$, melting at 129° , is obtained by the action of phenacyl bromide on ethylic sodioacetoacetate, and separated, along with the isomeride, by treating the product with cold, six per cent., aqueous potash, in which they do not dissolve; it is more conveniently prepared, however, by the method which Fritz describes for obtaining the isomeride melting at 161° (this vol., i, 152), namely, treatment of an ice-cold, alcoholic solution of bromoacetophenone with sodium and alcohol. The authors have found that the sole product of this action is the modification of low melting point; only after protracted boiling has the less fusible form been obtained by this method, and then only in quantity amounting to one-third of the whole product. The explanation of this discrepancy is probably to be found in the fact that the modification of low melting point is converted into the isomeride when the alcoholic solution is boiled.

Bromodiphenacyl, melting at 161° , has been already described by Fritz (*loc. cit.*), and, owing to the discrepancy indicated, is most conveniently obtained by the action of phenacyl bromide on ethylic sodioacetoacetate.

M. O. F.

Diduroquinone. By LEOPOLD RÜGHEIMER and M. HANKEL (*Ber.*, 1896, **29**, 2176—2185).—Duroquinone (see this vol., i, 677), on

treatment with a 5—10 per cent. alcoholic potash solution at the ordinary temperature is slowly polymerised to *diduroquinone*, $C_6Me_3O_2 \cdot CH_2 \cdot C_6Me_3O \cdot OH$, which crystallises from its alcoholic solution in small, yellow needles, melts at $202-203^\circ$, is only sparingly soluble in cold alcohol and benzene, but dissolves in alcoholic potash yielding a violet solution; it is not acted on when heated at 100° with alcohol previously acidified with hydrogen chloride, or by prolonged heating with alcoholic potash.

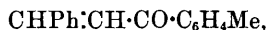
Diduroquinone ethylic ether, $C_{20}H_{23}O_3 \cdot OEt$, obtained by heating a solution of the diquinone in alcoholic potash with ethylic iodide, crystallises in yellow needles, and melts at $128-130^\circ$; it is not acted on by acetic anhydride at 190° , and, on reduction with zinc dust and acetic acid yields duroquinol. *Diduroquinone methylic ether* crystallises from hot alcohol in small, yellow needles, and melts at 126° . *Diduroquinone propylic ether* melts at 116° . *Acetyldiduroquinone*, obtained by the action of acetic anhydride on the diquinone, crystallises from its alcoholic solution with 1 mol. of alcohol; it loses half this alcohol at 100° , but does not lose the other $\frac{1}{2}$ mol. at 120° . The air-dried crystals melt at $128-132^\circ$, when dried at 100° they melt at $133-134^\circ$. *Benzoyldiduroquinone* melts at $140-142^\circ$.

Diduroquinone, when reduced in alcoholic solution with aluminium amalgam, yields a *dihydro*-derivative, which is rapidly oxidised again to the diquinone by contact with the air; on treatment with acetic anhydride, it yields a *monacetyl* derivative melting at 153° .

J. J. S.

Action of Benzaldehyde on Paratolyl Methyl Ketone. By STANISLAUS VON KOSTANECKI and G. ROSSBACH (*Ber.*, 1896, 29, 2245—2247; compare this vol., i, 556).—Dibenzylidenetriacetophenone is formed with great ease, even in the presence of dilute aqueous soda, if this reagent is allowed to act on the mixture for a considerable time. Paratolyl methyl ketone, on the other hand, does not form the tri-compound nearly so readily.

Paratolyl styryl ketone (paratolyl benzylidenemethyl ketone),



crystallises in long, thick needles, melts at 77° , and boils at 355° . Sulphuric acid colours it yellow. *Diparatolyl benzylidenedimethyl diketone*, $CHPh(CH_2 \cdot CO \cdot C_6H_4Me)_2$, forms vitreous prisms melting at $115-116^\circ$. It yields a colourless solution in sulphuric acid, which, however, soon becomes yellowish, and takes a greenish fluorescence. *Dibenzylidenetrimethyl triparatolyl triketone*,



is a crystalline powder, which melts at 228° , and is only sparingly soluble in alcohol. It dissolves in sulphuric acid, forming a red solution which has a cinnabar-red fluorescence.

A. H.

Action of Furfuraldehyde on Acetophenone. By STANISLAUS VON KOSTANECKI and L. PODRAJANSKY (*Ber.*, 1896, 29, 2248—2250).—Furfuraldehyde acts on acetophenone in a manner similar to benzaldehyde. *Furfurylideneacetophenone*, $C_4OH_3 \cdot CH:CH \cdot COPh$, is a thick,

yellowish oil, which boils at 317° , and is coloured brown by sulphuric acid. *Furfurylidenediacetophenone*, $C_4OH_3 \cdot CH(CH_2 \cdot C_6H_5)_2$, crystallises in lustrous, prismatic needles, melting at 95° . It dissolves in sulphuric acid forming a reddish-yellow solution, the coloration being probably due to the presence of the following compound.

Difurfurylidenetriacetophenone, $COPh \cdot CH[CH(C_4OH_3) \cdot CH_2 \cdot COPh]_2$, like the corresponding benzaldehyde compound, exists in two isomeric modifications. When a mixture of an alcoholic solution of acetophenone and furfuraldehyde with aqueous soda and alcohol is allowed to remain at the ordinary temperature, the compound obtained crystallises out in white needles; it melts at 175° , and forms a brownish-red solution in sulphuric acid. If, on the other hand, the mixture be heated, the product crystallises in thin, quadratic prisms, melts at $211-212^{\circ}$, and yields a brown solution in sulphuric acid.

Furfurylidenemethyl paratolyl ketone forms yellow needles, melts at 67° , boils at 330° , and yields a yellow solution with sulphuric acid. *Furfurylidenedimethyl diparatolyl diketone*, $C_4OH_3 \cdot CH(CH_2 \cdot CO \cdot C_6H_4Me)_2$, crystallises in lustrous needles, melting at $112-113^{\circ}$, and yielding a yellow solution in sulphuric acid.

A. H.

4 : 5-Diphenyloctane-2 : 7-dione. By CARL D. HARRIES and G. ESCHENBACH (*Ber.*, 1896, **29**, 2121—2127; compare this vol., i, 305).—Owing to the production of benzylacetone when benzylideneacetone is reduced, it seemed possible that the substance arising from diphenyl-4 : 5-octanedione-2 : 7 (*loc. cit.*) under the influence of sodium ethoxide, is due to the combination of that substance with unchanged benzylideneacetone; such a result would be analogous to the action of ethylic acetoacetate on benzylideneacetone (*Abstr.*, 1894, i, 528), or the condensation of benzylideneacetone with benzylidenediacetone (this vol., i, 557). Attempts to produce the compound in question by the action of sodium ethoxide on a mixture of benzylacetone and benzylideneacetone, have, however, been unsuccessful, and this circumstance, taken in conjunction with the behaviour of the substance towards oxidising agents and bromine, appears to indicate that the original view of its formation is the correct one.

1 : 2-Dimethyl-4 : 5-diphenylhexamethylene, $\begin{array}{c} CHPh \cdot CH_2 \cdot CHMe \\ CHPh \cdot CH_2 \cdot CHMe \end{array}$, is obtained by reducing diphenyl-4 : 5-octanedione-2 : 7 in alcoholic solution with zinc and hydrochloric acid; it crystallises from light petroleum in transparent crystals belonging to the triclinic system, and melts at 97° , boiling unchanged at 270° .

Diphenyl-4 : 5-octanedione-2 : 7 resists the action of gentle oxidising agents, yielding benzoic acid under more vigorous treatment. Concentrated nitric acid gives rise to a substance which melts indefinitely at $120-135^{\circ}$, and which the authors regard as a mixture of isomeric dinitrobenziles, $C_2O_2(C_6H_4NO_2)_2$. Bromine gives rise to hexabromodiphenyl-4 : 5-octanedione-2 : 7, stilbene dibromide, hexabromostilbene, tetrabromacetone, and pentabromacetone.

Hexabromodiphenyl-4 : 5-octanedione-2 : 7, crystallises from glacial acetic acid in small, white needles, and melts at $190-191^{\circ}$.

M. O. F.

Dithienylphenylmethane and its Nitro-derivatives. By ALBERT TÖHL and A. NAHKE (*Ber.*, 1896, **29**, 2205—2207).—*Dithienylphenylmethane*, $\text{CHPh}(\text{C}_4\text{SH}_3)_2$, is best prepared by the following method:—Thiophen (17 grams) and benzaldehyde (10 grams) are mixed with 50 grams of light petroleum and 20 grams of phosphoric anhydride, and the mixture left for several hours; after the reaction is over, water is added, and the whole is extracted several times with light petroleum; the extract is washed with alkali, dried, and fractionated. The crystalline fraction is dissolved in a little boiling alcohol, and ether added until drops of oil cease to be thrown down. The dithienylphenylmethane then crystallises in colourless needles, which melt at $74-75^\circ$. With isatin and sulphuric acid, it gives a brownish-red colour, which changes to green on warming. The same dithienylphenylmethane may be obtained by the following methods, the yield, however, is not good. (1) By heating a mixture of benzaldehyde and thiophen at 100° for several hours. (2) By heating a mixture of thiophen and benzaldehyde to boiling in the presence of zinc chloride. (3) By the action of sulphuric acid on a mixture of benzaldehyde and thiophen. (4) By the action of aluminium chloride on a mixture of benzylidene chloride and thiophen.

Dithienylmetanitrophenylmethane, obtained by the action of phosphoric anhydride on a solution of thiophen and metanitrobenzaldehyde in ether and chloroform, crystallises from light petroleum in plates which have a pearly lustre, melts at $72-73^\circ$, and is readily acted on by fuming nitric acid.

Dithienylorthonitrophenylmethane crystallises in needles and melts at 84° , and *dithienylparanitrophenylmethane* melts at $89-90^\circ$.

J. J. S.

[**Coloured Rosaniline Bases.**] By GEORG VON GEORGIEVICS (*Ber.*, 1896, **29**, 2015—2016; compare this vol., i, 441).—The author has examined the precipitate, described by him as a coloured rosaniline base, for chlorine, and finds that no chlorine is present when it is purified by washing with water. The small amount of chlorine in the crude precipitate is due to sodium chloride, and not as Weil has suggested (this vol., i, 565) to a basic rosaniline hydrochloride.

A. H.

Oxidation by means of Hydroxylamine Hydrochloride. By HEINRICH BILTZ (*Ber.*, 1896, **29**, 2080—2082; compare E. von Meyer, *Abstr.*, 1884, 1187; and Nietzki and Benckiser, *Abstr.*, 1886, 450).—When triphenylvinyl alcohol (2 grams) is boiled with hydroxylamine hydrochloride ($3\frac{1}{2}$ grams) and absolute alcohol (30 grams) for 12 hours, it yields *phenylbenzoïn ethylic ether*. This is formed by the addition of the elements of alcohol, and the subsequent oxidation of the secondary alcoholic group thus formed. It crystallises in well developed rhombic crystals resembling those of barytes. It yields no derivatives with hydroxylamine, phenylhydrazine, semicarbazide, or aniline; this inactivity is probably due to stereochemical influences (compare Beckmann, *Annalen*, **252**, 74). That the reaction proceeds according to the equation $\text{C}_{20}\text{H}_{16}\text{O} + \text{C}_2\text{H}_5\text{OH} + \text{NH}_4\text{OCl} = \text{C}_{22}\text{H}_{16}\text{O}_2 + \text{H}_2\text{O} + \text{NH}_4\text{Cl}$, was proved by estimating the amount of ammonium chloride formed from a given

weight of hydroxylamine hydrochloride. On hydrolysis with soda, the phenylbenzoin ethylic ether is decomposed into benzoic acid and benzhydrol ethylic ether. J. J. S.

Diphenyldiphenylenepinacolin and Tetraphenylenepinacolin. By HEINRICH KLINGER and CARL LONNES (*Ber.*, 1896, **29**, 2152—2156; compare this vol., i, 374; also Graebe and Stindt, this vol., i, 565).—*Diphenyldiphenylenepinacolin*, $\begin{smallmatrix} \text{C}_6\text{H}_4 \\ | \\ \text{C}_6\text{H}_4 \end{smallmatrix} > \text{CPh} \cdot \text{COPh}$, is

obtained by oxidising diphenyldiphenylenethylene (Kaufmann, this vol., i, 242), and also from triphenylmethane, benzoic chloride, and potassium (compare Hanriot and St. Pierre, *Abstr.*, 1889, 882). It separates from acetone in colourless, highly refractive crystals, and melts at 172° ; the crystals are monoclinic, $a : b : c = 0.7086 : 1 : 1.2513$, $\beta = 59^\circ 9' 40''$. The substance undergoes no change when heated with benzoic anhydride or acetic chloride at 150 — 160° , but yields benzoic acid and phenyldiphenylenemethane under the influence of phenylhydrazine or alcoholic potash. The *hydrocarbon*, $\text{C}_{26}\text{H}_{18}$, is obtained from diphenyldiphenylenepinacolin by the action of hot, fuming hydriodic acid, and crystallises in needles melting at 235° ; oxidation converts it into the *compound*, $\text{C}_{26}\text{H}_{18}\text{O}_2$, which melts at 168° . Hanriot and St. Pierre obtained the same hydrocarbon, ascribing to it the formula $\text{C}_{26}\text{H}_{20}$; the hydrocarbon, $\text{C}_{26}\text{H}_{22}$, obtained by these investigators from potassium triphenylmethane and benzylic chloride, is regarded by the authors as *unsymmetrical diphenyldiphenylenethane*, $\begin{smallmatrix} \text{C}_6\text{H}_4 \\ | \\ \text{C}_6\text{H}_4 \end{smallmatrix} > \text{CPh} \cdot \text{CH}_2\text{Ph}$ (compare this vol., i, 375).

Tetraphenylenepinacolin, $\begin{smallmatrix} \text{C}_6\text{H}_4 \\ | \\ \text{C}_6\text{H}_4 \end{smallmatrix} > \text{C} < \begin{smallmatrix} \text{CO} \\ | \\ \text{C}_6\text{H}_4 \end{smallmatrix} > \text{C}_6\text{H}_4$, is obtained by treating an ethereal solution of fluorene ketone with acetic chloride and zinc dust, and is also produced on oxidising tetraphenylenethylene (compare Graebe and von Mantz, this vol., i, 442); it crystallises from benzene in colourless plates, melting at 258° (uncorr.), and is identical with bidiphenylenethylene oxide, obtained by Graebe and Stindt on heating the bromide of bidiphenylenethylene with water at 150° (this vol., i, 566). The authors advocate the foregoing expression for the constitution of tetraphenylenepinacolin in preference to the oxide formula already adopted (*loc. cit.*), owing to the properties of an *acid*, $\text{C}_{26}\text{H}_{18}\text{O}_2$, obtained by the action of alcoholic potash on the pinacolin. This substance, which melts at 243 — 244° , loses H_2O when heated at 340° , tetraphenylenepinacolin being regenerated; it is readily oxidised in alkaline solution, yielding the *acid*, $\text{C}_{26}\text{H}_{18}\text{O}_3$, which melts at 177 — 179° , this substance giving rise to the *lactone*, $\text{C}_{26}\text{H}_{16}\text{O}_2$, which melts indefinitely at 213 — 219° . Hydriodic acid converts tetraphenylenepinacolin into the *hydrocarbon*, $\text{C}_{26}\text{H}_{16}$, which crystallises in white needles, and melts at 215° . Bromine is without action on tetraphenylenepinacolin, which, on oxidation, yields the compound $\text{C}_{26}\text{H}_{16}\text{O}_2$, melting at 269° .

Tetraphenylenepinacone diacetate, $\begin{smallmatrix} \text{C}_6\text{H}_4 \\ | \\ \text{C}_6\text{H}_4 \end{smallmatrix} > \text{C}(\text{OAc}) \cdot \text{C}(\text{OAc}) < \begin{smallmatrix} \text{C}_6\text{H}_4 \\ | \\ \text{C}_6\text{H}_4 \end{smallmatrix}$,

is produced along with tetraphenylenepinacolin and tetraphenylenethylene when an ethereal solution of fluorene ketone is treated with acetic chloride and zinc dust; it crystallises from a mixture of benzene and alcohol in rosettes of leaflets, and melts at 270°, evolving gas. The same compound has been obtained by Graebe and Stindt (this vol., i, 566). Hydrolysis with alcoholic potash gives rise to fluorene ketone and fluorene alcohol, whilst 70 per cent. sulphuric acid at 100° converts it into tetraphenylenepinacolin.

M. O. F.

Diphenyldiphenylenethylene and Tetraphenylenethylene.

By HEINRICH KLINGER and CARL LONNES (*Ber.*, 1896, **29**, 3157—3158).—It has been already mentioned (this vol., i, 375) that diphenyldiphenylenethylene, a colourless hydrocarbon, yields deep yellow solutions; the property is exhibited in an equal degree by the hydrocarbon remaining after fractional oxidation, and on crystallising the picrate fractionally, and regenerating the hydrocarbon from three separations, products were obtained which exhibited, in 1 per cent. benzene solution, a yellow colour comparable with that of a 0.075 per cent. solution of potassium chromate. The authors consequently attribute the property in question to the pure hydrocarbon, which they regard, from this point of view, as occupying an intermediate position between colourless tetraphenylethylene and red tetraphenylenethylene.

Tetraphenylenethylene is obtained as a bye-product in reducing fluorene ketone with acetic chloride and zinc dust; it is identical with bidiphenylenethylene, described by Graebe (*Abstr.*, 1893, i, 38). It distils under diminished pressure without undergoing decomposition, and crystallises from benzene in beautiful red needles, which melt at 189—190° (uncorr.).

M. O. F.

γ -Amidonaphtholsulphonic acid. By ERNST TÄUBER and FRANZ WALDER (*Ber.*, 1896, **29**, 2267—2270).— γ -Amidonaphtholsulphonic acid is obtained by fusing 2-amidonaphthalene-3':1'-disulphonic acid with alkalis (German Patent 53,076). It forms white, sparingly soluble needles, and reduces ammoniacal silver solutions and Fehling's solution. Nitrous acid converts it into the *diazo-sulphonic acid*, which is itself converted by alkalis into a deep blue colouring matter, having the same composition as the diazo-sulphonic acid. This is not affected by cold sulphuric acid, but decomposes when heated with it. The diazosulphonic acid readily yields the corresponding *hydrazine-sulphonic acid*, which crystallises in fascicular groups of colourless needles; these become red on exposure to light.

When this hydrazinesulphonic acid is boiled with copper sulphate, it is converted into a naphtholsulphonic acid, which, on treatment with sodium amalgam, yields α -naphthol. It follows from this that the original γ -amidonaphtholsulphonic acid is the 2-amido-1'-hydroxynaphthalene-3'-sulphonic acid.

A. H.

Isomeric Naphthalene Derivatives. IV. Diamidonaphthalenesulphonic acids. By PAUL FRIEDLÄNDER and W. H. KIEL-

BASINSKI (*Ber.*, 1896, **29**, 1978—1983).—The object of this research was to investigate the effect of the presence of the sulphonic group on the basicity of the naphthylenediamines. 1 : 2-Naphthylenediamine-4-sulphonic acid does not possess basic properties, and is less soluble in dilute hydrochloric acid than in water. 1 : 3'-Naphthylenediamine-4-sulphonic acid is prepared by the action of ammonia on 1 : 3'-amidonaphthol-4-sulphonic acid (German Patent, 77,157). The latter forms slender, sparingly soluble needles. It is converted by the action of sodium amalgam into 1 : 3'-amidonaphthol. 1 : 3'-Naphthylenediamine-4-sulphonic acid forms sparingly soluble needles, and acts as a monacid base, the *platinochloride*, $[C_{10}H_5(NH_2)_2SO_3H]_2 \cdot H_2PtCl_6$, crystallising in yellow prisms. The *ammonium salt* crystallises in nacreous plates, whilst the *sodium salt* is less soluble, and forms tablets.

1 : 3'-Naphthylenediamine-4 : 1'-disulphonic acid is obtained by the reduction of the corresponding nitro-compound (Kalle & Co., German Patent, 72,665). When its tetrazo-derivative is boiled with cuprous chloride, it yields the *monosodium salt* of 1 : 3'-dichloronaphthalene-4 : 1'-disulphonic acid, which crystallises in yellowish needles, the *normal silver salt* crystallising in slender, readily soluble needles. The acid is converted by distillation with dilute sulphuric acid into 1 : 3'-dichloronaphthalene. Sodium amalgam, moreover, converts the naphthylenediaminedisulphonic acid into 1 : 3'-naphthylenediamine.

1 : 3'-Naphthylenediamine-4 : 1'-disulphonic acid crystallises in sparingly soluble needles, and does not possess basic properties, the introduction of the second sulphonic group into the ring, which only contained an amido-group in the acid last described, having thus destroyed the basic properties which were shown by that acid. 1 : 3'-Naphthylenediamine-3 : 1'-disulphonic acid is formed along with the foregoing acid, but can be separated from it by the different solubility of its sodium salt; its constitution was determined in the same way as that of its isomeride. The dichloronaphthalenedisulphonic acid yields a readily soluble monosodium salt and a less soluble normal salt. The acid has no basic properties. 1 : 4-Naphthylenediamine-2-sulphonic acid (L. Cassella & Co., German Patent, 70,890) is sparingly soluble in water, whilst the ammonium and sodium salts are readily soluble; this acid has well marked basic properties, and yields a crystalline, sparingly soluble *hydrochloride*, and an almost insoluble *sulphate*. A. H.

New Method for Hydroxylating in the Anthraquinone Series. By LEONHARD WACKER (*J. pr. Chem.*, 1896, [2], **54**, 88—94).—Anthraquinone and hydroxyanthraquinones may be hydroxylated by treatment with persulphates in sulphuric acid solution. The higher hydroxylated compounds are obtained by this method in the form of their sulphates, characterised by their solubility in water and their conversion into polyhydroxyanthraquinones when heated with sufficiently concentrated sulphuric acid. The formation of the higher hydroxylated compounds is conditioned by the ability of the sulphuric acid to act as a substituting agent; thus, if acid of 66° B. is used, or a feebly fuming acid, at low temperatures, lower

hydroxylated dyes are exclusively formed, however much persulphate is used.

The paper contains details of proportions to be employed in particular cases, most of which have appeared in patent specifications. The following table gives a general view of the kind of results obtained.

Raw material.	Conditions of working.			
	Sulphuric acid of 66° B., and about 2 parts of persulphate.	In feebly fuming sulphuric acid.		
		At 20—50°, with 1—2 parts of persulphate.	At 80—150°.	
			With 2 parts of persulphate.	With 4 parts and upwards of persulphate.
Anthraquinone ..	Monohydroxyanthraquinone	Partial action with formation of cyanin	Partial action with formation of cyanin	Cyanin.
Alizarin	No apparent action	Purpurin.....	more violet dye	Cyanin.
Anthrapurpurin..	Hydroxyanthrapurpurin	Hydroxyanthrapurpurin	more violet dye	Cyanin.
Flavopurpurin ...	Hydroxyflavopurpurin	Hydroxyflavopurpurin	more violet dye	Cyanin.
Anthrachryson..	—	—	—	Cyanin.

Ammonium persulphate is generally used.

The conversion of β -hydroxyanthraquinone into quinizarin by this method is of theoretical interest as involving a migration of a hydroxyl group.

A. G. B.

Crystallographic Properties of Alkylcamphors of the Aromatic Series. By JULES MINGUIN (*Compt. rend.*, 1896, 123, 248—249).—*Benzylcamphor* forms rhombic prisms of 99°05'. For $b = 1000$, $h = 857$. The only modification is a^1 , which is developed to such an extent as to extinguish p .

Anisylcamphor forms prisms of 105° 45' in which $b = 1000$, $h = 675\cdot1$, the faces commonly observed being $m, g^1, g^3, a^1, e^1, b^1$, the domes and the faces g^3 being, as a rule, highly developed.

Methylsaligenylcamphor, isomeric with anisylcamphor, does not crystallise distinctly, but seems to belong to the rhombic system.

Ethylsaligenylcamphor forms rhombic prisms with an angle of 110°; $b = 1000$, $h = 222\cdot9$. The faces observed are m, g, g^3, h^1, e^1, a^1 , but the faces a^1 are often wanting, owing to the development of the faces e^1 .

In no case were hemihedral faces observed. The crystalline similitude previously referred to is also observed in the reduction derivatives, and an angle of about 160° corresponding with a face g^3 is found in the zone mm' , and this is connected with the observed constancy of the angle of the prism. The same angle of 160° occurs in the bromine derivatives obtained from benzylidene and the benzylcamphors. Further, the products of reduction are all rhombic, even when the original compound is monoclinic, and the two atoms of hydrogen seem to have a special influence in modifying the domes in such a manner as to increase the symmetry. C. H. B.

Camphoric Mononitrile, its Anhydride and Anilide. By ALBIN HALLER and JULES MINGUIN (*Compt. rend.*, 1896, **123**, 216—220).—By the action of acetic chloride on camphoroxime, the authors have obtained a compound, $C_{20}H_{28}N_2O_3$, and an acid, $C_{10}H_{15}NO_2$, which in all probability are identical with the compounds obtained by Oddo and Leonardi (*Gazzetta*, **26**, i, 405) in the same way from a camphoroxime prepared in a somewhat different manner.

The acid $C_{10}H_{15}NO_2$ is converted into camphoric acid and ammonia when treated with concentrated aqueous potash, and hence must be regarded as camphoric mononitrile. The compound $C_{20}H_{28}N_2O_3$ is the anhydride of this acid, into which it is converted by the action of alcoholic potash, and from which it can be obtained by heating with a molecular proportion of phenylic isocyanate below 100° , the other products being carbonic anhydride and diphenylcarbamide. If the mixture of anhydride and diphenylcarbamide thus produced is heated above 160° , there is a further evolution of carbonic anhydride, and the anilide of camphoric mononitrile, $CN \cdot C_6H_{14} \cdot CO \cdot NHPh$, is produced.

The specific rotatory powers of the mononitrile, anhydride, and anilide are $+67.70$, $+54.66$, and $+62.6$ respectively, and their melting points are 149 — 150° , 175 — 176° , and 197° .

The formation of camphoric mononitrile from camphoroxime may be explained by assuming that the NOH group has the same influence as any other negative radicle introduced into the methylene of the

$\begin{array}{c} CH_2 \\ | \\ < CO \end{array}$ group, and renders the union between the methylene and the carbonyl groups very unstable, with the result that $C_8H_{14} \begin{array}{c} C: NOH \\ | \\ CO \end{array}$

becomes $CN \cdot C_8H_{14} \cdot COOH$. The anhydride is a secondary product of the action of the excess of acetic chloride on the acid. This view is supported by the facts that cyanocamphor is readily converted into cyanocampholic acid, and that the latter yields an anhydride when heated with phenylic isocyanate. C. H. B.

Camphoric acid. III. By WILLIAM A. NOYES (*Ber.*, 1896, **29**, 2326—2328; compare *Abstr.*, 1895, i, 295 and 552).—According to Tiemann's formula for camphoric acid (*Abstr.*, 1895, i, 428), the carboxylic group in amidodihydrocampholytic and amidolauronic

acids should be secondary, and the same velocity of etherification would be then exhibited by both acids; it is found, however, that the action of boiling alcohol in presence of sulphuric acid converts into ethylic salt 10 times as much of the former acid as of the latter, and it therefore appears that amidodihydrocampholytic acid contains a secondary carboxylic group, whilst in amidolauronic acid this complex is tertiary.

Hydroxylauronic acid, $\text{OH}\cdot\text{C}_8\text{H}_{14}\cdot\text{COOH}$, is obtained from ethylic amidolauronate by the action of nitrous acid, ethylic isolauronate (Walker's allocampholytic acid) being also formed; it is a viscous liquid, and dissolves with some difficulty in water. The *copper* salt is a bright green powder, which dissolves sparingly in water; it contains $1\text{H}_2\text{O}$. Chromic acid oxidises hydroxylauronic acid in the cold, producing a ketone and carbonic anhydride; it appears probable, therefore, that the substance in question is a β -hydroxy-acid, the hydroxyl group corresponding with the amido-group in amidolauronic acid, and one of the carboxylic groups in camphoric acid, which the author regards as a derivative of succinic acid.

Fresh evidence in favour of the view that *cis*-campholytic acid (Abstr., 1895, 552) is an $\alpha\beta$ -unsaturated acid, is afforded by converting it into dihydro-*cis*-campholytic acid by means of amylic alcohol and sodium, and treating with alcoholic potash the α -bromodihydro-*cis*-campholytic acid obtained from it, when *cis*-campholytic acid is regenerated quantitatively.

The amide of dihydro-*cis*-campholytic acid is converted by sodium hypobromite into an *amine*, $\text{C}_8\text{H}_{15}\cdot\text{NH}_2$, which boils at $156\cdot5^\circ$, and has the sp. gr. $0\cdot8431$ at $20^\circ/20^\circ$. Nitrous acid converts this base into the *hydrocarbon*, C_8H_{14} , and the secondary *alcohol*, $\text{C}_8\text{H}_{15}\cdot\text{OH}$; the latter is oxidised by chromic acid to a *ketone*, the *oxime* of which crystallises from alcohol in needles or prisms, and melts at $112\text{--}113^\circ$. According to Kipping, the melting point of dimethyl-1:3-cyclohexanone-2 is $114\text{--}115^\circ$, whilst Zelinsky describes this substance as melting at $104\text{--}105^\circ$; the author has prepared it by another method in a form melting at $120\text{--}122^\circ$, and it is therefore uncertain whether this substance is identical with the foregoing oxime. M. O. F.

Vicin, a Glucoside. By C. HEINRICH L. RITTHAUSEN (*Ber.*, 1896, 29, 2108—2109).—Although vicin is described as an alkaloid in Beilstein's Handbook, the author has shown that this substance is a glucoside. Hydrolysis with dilute sulphuric acid gives rise to divicin and a mixture of glucose and galactose. M. O. F.

Hydroxy-2'-phenylindole and Nitrosobenzoic acid. By EMIL FISCHER (*Ber.*, 1896, 29, 2062—2064).—The name hydroxy-2'-phenylindole has been substituted for phenylindoxyl, the name previously given to the substance obtained from benzoïnoxime by the elimination of water (Abstr., 1895, i, 371). Its constitution must be either $\text{HN}\langle\text{C}^{\text{Ph}}_{\text{C}_6\text{H}_4}\rangle\text{C}\cdot\text{OH}$ or $\text{OH}\cdot\text{N}\langle\text{C}^{\text{Ph}}_{\text{C}_6\text{H}_4}\rangle\text{CH}$. On oxidation with dilute potassium permanganate in the cold, it yields orthonitrosobenzoic acid and benzoylanthranilic acid. No definite conclusions as to

the constitution of the hydroxyindole can be drawn from these products of oxidation.

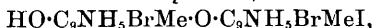
Orthonitrosobenzoic acid is best separated from benzoylanthranilic acid as follows: The mixture of the two is dissolved in ammonia, the benzoylanthranilic acid is precipitated by acidifying, and the mother liquor is then extracted some 10 times with ether. The ethereal solution, on concentration, yields the nitroso-acid, whilst a considerable quantity of benzoic acid still remains in solution. After recrystallisation from boiling absolute alcohol, orthonitrosobenzoic acid forms almost colourless crystals, but it turns brown above 180° , and is completely decomposed at about 210° . The acid is extremely sparingly soluble in cold alcohol and ether, but more readily in hot alcohol and in glacial acetic acid, yielding green solutions. The ammoniacal solution is also coloured green. It is readily reduced to anthranilic acid by dissolving in ammonia, then saturating the solution with hydrogen sulphide, and finally heating at 100° for an hour in sealed tubes. J. J. S.

Alkylloxides of 1-Hydroxyquinoline. By ADOLPH CLAUS and EMIL MOHL (*J. pr. Chem.*, 1896, **54**, 1—17).—1-*Hydroxyquinoline methosulphate*, $(C_9NH_5OH)_2Me_2SO_4 + 3H_2O$, is prepared by heating an aqueous alcoholic solution of the methiodide with the calculated quantity of silver sulphate in a reflux apparatus; it crystallises from the concentrated filtrate in large, lustrous, golden-yellow prisms, melts at 226° , and dissolves freely in water, but more sparingly in alcohol. As has been indicated already (Abstr., 1892, 877), it is not possible to produce from this methosulphate an "intermediate product" such as is obtainable from the methiodide by treatment with alkalis (Abstr., 1890, 1323); however small a proportion of alkali is used, an equivalent proportion of the methosulphate is converted into the methohydroxide, the rest remaining unchanged.

1-*Hydroxyquinoline methodichromate*, $(C_9NH_5OH)_2Me_2Cr_2O_7 + 2H_2O$, is precipitated in the form of dark yellow, small, lustrous needles when potassium dichromate is added to a solution of the methiodide; it is sparingly soluble in alcohol and water, and decomposes at 80° . The *methoxalate*, $(C_9NH_5OH)_2Me_2C_2O_4 + H_2O$, prepared by neutralising a solution of the methohydroxide, evaporating to dryness, dissolving in absolute alcohol, and adding ether, forms dark yellow, lustrous, slender crystals; it melts at 151° , and dissolves freely in water, but more sparingly in alcohol. Neither of these two salts yields an "intermediate product," and this seems to be generally the case with the salts of oxy-acids.

1-Hydroxyquinoline ethobromide crystallises with $1\frac{1}{2}H_2O$, not $2\frac{1}{2}$ (Abstr., 1893, i, 484), and the crystals melt at 72° . The benzochloride (*loc. cit.*) crystallises with $1\frac{1}{2}H_2O$.

4 : 1-*Bromhydroxyquinoline methiodide*, prepared by heating its components (Abstr., 1892, 354) for 6—8 hours in a sealed tube at 130 — 135° , crystallises in golden-yellow, lustrous laminæ, with $1H_2O$, and melts at 157° . By treatment with half an equivalent of an alkali, it yields the "intermediate product,"



in the form of small, brilliant, blood-red crystals, which melt at 182° . The *methohydroxide*, which is formed when excess of alkali is used, crystallises in large, lustrous, brownish-red prisms, and melts at 180° .

Besides the two methods by which 1-methoxyquinoline methiodide has been prepared (Abstr., 1890, 1323), a third is available, namely, the action of methylic iodide on the inner anhydride of 1-hydroxyquinoline methohydroxide; this compound, C_9NH_5MeO [$O = 1 : 1'$], was prepared by heating the methohydroxide (which crystallises with $2H_2O$, not $1H_2O$; Abstr., 1892, 877) at $70-80^{\circ}$ in a current of air. All three methods yield the same compound.

1-Ethoxyquinoline methiodide is prepared in the usual way from its components, but cooling is essential; it crystallises in thick, transparent, bright yellow prisms, melts at 200° , and is soluble in hot water or alcohol. When treated with silver chloride, the corresponding *methochloride* is obtained; this crystallises in nearly colourless, lustrous prisms and needles with $2H_2O$, and melts at 107° . When the methiodide is treated with alkalis, it yields a base, which is soluble in ether, and is probably the corresponding alkylenequinolinium base (compare Abstr., *loc. cit.*); in this respect, the 1-alkyloxyquinoline alkyl haloid salts resemble the 3-derivatives. With silver oxide, however, the resemblance between the 1- and the 3-derivatives is not maintained; when an aqueous solution of 3-ethoxyquinoline methochloride is shaken with ether and silver oxide, the methohydroxide is formed and remains dissolved in the water; similar treatment of an aqueous solution of 1-ethoxyquinoline methochloride produces the base, which is soluble in ether, so that the water retains none.

A. G. B.

Reduction Products from Cinchomeric acid and from Apophyllenic acid. By WILHELM KOENIGS and FRITZ WOLFF (*Ber.*, 1896, 29, 2187—2192; compare this vol., i, 251).—When methylic cinchomerate is reduced with sodium and alcohol, it yields an ethereal salt of hexahydrocinchomeric acid. The reduced mixture is best hydrolysed by repeated evaporation to dryness with dilute hydrochloric acid, and the hydro-acid separated from the unaltered acid by conversion into its nitrosamine; the latter may then be extracted with ether and converted into the acid.

The *hydrochloride* of the hexahydro-acid crystallises in anhydrous forms, melts at 237° , is readily soluble in cold water, and sparingly in cold alcohol. Its *aurochloride* melts at 205° , and on boiling in aqueous solution readily decomposes and yields metallic gold.

Hexahydrocinchomeric acid melts at 256° , and is readily soluble in water. It is a monobasic acid, but its nitrosamine is dibasic. Its *calcium* salt crystallises with $5H_2O$, and is readily soluble in water. The *nitrosamine* is an oil, and yields a readily soluble *barium* salt, a gelatinous *silver* salt, and a crystalline *strychnine* salt. The hexahydro-acid is not acted on when boiled with a solution of sodium in amyl alcohol (compare Besthorn, this vol., i, 252).

Apophyllenic acid (methylbetaincinchomeric acid; Vongerichten, Abstr., 1880, 110) is best obtained from cotarnine (Roser,

Annalen, **254**, 354). This is first heated with phosphorus pentachloride at 160–170°, then treated with ice, and, after boiling with water, filtered; the filtrate is evaporated to dryness, and the tarry residue oxidised with a mixture of concentrated nitric acid and water. Apophyllenic acid, when reduced with tin and concentrated hydrochloric acid, yields *n-methylhexahydrocinchomeric acid*; this is best purified by conversion into its ethylic salt, which can be extracted with ether. The acid, which crystallises slowly from its concentrated aqueous solutions, can also be precipitated by adding alcohol. It melts and decomposes at 206–207°. J. J. S.

Synthesis of 3'-Propylisoquinoline. By JACQUES M. ALBAHARY (*Ber.*, 1896, **29**, 2391–2398).—The synthesis was effected by the method introduced by Gabriel and Neumann (*Abstr.*, 1892, i, 228). *ψ-Dibutrylorthocyanobenzyl cyanide*, $\text{CN} \cdot \text{C}_6\text{H}_4 \cdot \text{C}(\text{CN}) : \text{CPr} \cdot \text{O} \cdot \text{COPr}$, obtained by heating orthocyanobenzyl cyanide with butyric anhydride and sodium butyrate, crystallises in slender, matted needles, melting at 105°. When it is heated with alcoholic potash, it yields

4' : 3'-cyanopropylisocarbostyryl, $\text{C}_6\text{H}_4 < \begin{array}{c} \text{C}(\text{CN}) : \text{CPr} \\ \text{CO} - \text{NH} \end{array}$, which crystallises

in slender needles melting at 221°. A small amount of a substance which melts at 80°, and has the composition $\text{C}_{15}\text{H}_{16}\text{N}_2\text{O}$, is also formed. Cyanopropylisocarbostyryl is readily converted by boiling with sulphuric acid and water into *propylisocarbostyryl*, which crystallises in yellowish needles, melting at 130–131°. When this substance is heated with phosphorus oxychloride, it yields 1' : 3'-chloro-

propylisoquinoline, $\text{C}_6\text{H}_4 < \begin{array}{c} \text{CH} : \text{CPr} \\ \text{CCl} : \text{N} \end{array}$, which is a yellow liquid, boiling

at 302–303° (pressure = 746 mm.). It has a characteristic odour, and is only a weak base. The *platinochloride* melts and decomposes at 195°, and the *aurochloride* melts at 140–141°. The halogen atom readily reacts with the sodium salts of compounds of alcohols and phenols. 1' : 3'-*Methoxypropylisoquinoline* is a yellowish oil, which boils at 281°. The *picrate* melts at 130–134°; the *platinochloride* melts and decomposes at 169–170°, and the *aurochloride* at 130–132°. The *chromate* is a thick, reddish-brown oil. 1' : 3'-*Ethoxypropylisoquinoline* boils at 287°; the *picrate* melts at 130°, and the *platinochloride* decomposes at 178–182°. 1' : 3'-*Phenoxypropylisoquinoline* is an unstable oil, which has not been obtained pure. The *picrate* melts at 96–98°.

Chloropropylisoquinoline is reduced by hydriodic acid and phosphorus at 160–170°, and is thus converted into 3'-*propylisoquinoline*, $\text{C}_6\text{H}_4 < \begin{array}{c} \text{CH} : \text{CPr} \\ \text{CH} : \text{N} \end{array}$; this has a characteristic pleasant odour, boils at 271°, and has the sp. gr. 1.01561 at 24°. The *picrate* melts at 161°; the *aurochloride* melts and decomposes at 115°; whilst the *platinochloride* decomposes at 189° without melting. A. H.

Correction [Pyrazolone Derivatives]. By WILHELM AUTENRIETH (*Ber.*, 1896, **29**, 2169–2171).—The author points out that the azo-compound melting at 155°, obtained by the action of ethylic

β -chlorocrotonate on phenylhydrazine (this vol., i, 627), is identical with Knorr's phenylhydrazone of phenylmethyl-4-ketopyrazolone (Abstr., 1888, 724).

The dibenzoyl derivative of bisphenylmethylpyrazolone (this vol., i, 627) is identical with Nef's benzoyl derivative of bis-1 : 2 : 3-phenylbenzoylmethylpyrazolone (Abstr., 1892, 146). Although previously described by the author as melting at 189—190°, a re-examination shows that its melting point is 194—196°; Nef states that the substance melts at 203°.

M. O. F.

Ethylic Mono- and Di-phenacetylmalonate, and the Action of Phenylhydrazine on Ethereal Salts of Acidyl Derivatives of Malonic acid. By HEINRICH SCHOTT (*Ber.*, 1896, **29**, 1985—1996).—Phenacetic chloride reacts with ethylic sodiomalonate, free from alcohol, to form a mixture of the mono- and di-derivatives. *Ethylic phenacetylmalonate* is a colourless liquid which dissolves readily in aqueous soda, and in aqueous solution gives a red coloration with ferric chloride. *Ethylic diphenacetylmalonate* is insoluble in dilute soda, and in alcoholic solution gives no coloration at first with ferric chloride, although a coloration is produced when the solution is allowed to remain, the monophenacetyl derivative being formed. These two substances are accompanied by a third of unknown constitution, which is only formed in small quantity, has the formula $C_{12}H_{10}O_3$, and melts at 114—117°.

Phenylhydrazine reacts with ethylic phenacetylmalonate in two ways. One portion is decomposed with formation of phenacetylphenylhydrazide and ethylic malonate, whilst the other forms a pyrazolone. *Ethylic 1 : 3 : 5-phenylbenzylpyrazolone-4-carboxylate*, $NPh \begin{smallmatrix} N : C \cdot CH_2Ph \\ \diagup \\ CO \cdot CH \cdot COOEt \end{smallmatrix}$, which is thus produced, crystallises in colourless prisms melting at 124—127°. Ferric chloride produces a deep violet coloration. The same products are formed from ethylic diphenacetylmalonate, one of the phenacetyl groups being first eliminated as phenacetylphenylhydrazide.

Ethylic acetylmalonate yields with phenylhydrazine an unstable compound melting at about 80°, which has not been obtained pure, but is probably the hydrazone. No acetylphenylhydrazide is formed. Ethylic diacetylmalonate, on the other hand, yields β -acetylphenylhydrazide and *ethylic 1 : 3 : 5-phenylmethylpyrazolone-4-carboxylate*, which forms a crystalline powder, and melts at 119—121.5°. It is probably this substance which was described by Michael as the hydrazone (Abstr., 1888, 1054).

A. H.

Azonium Compounds from β -Naphthaquinonesulphonic acid and Phenylorthophenylenediamine. By FRIEDRICH KEHRMANN and E. LOCHER (*Ber.*, 1896, **29**, 2072—2075).—Böniger's 1 : 2-naphthaquinone-4-sulphonic acid readily reacts in dilute acid solutions with phenylorthophenylenediamine to form the two isomeric azonium compounds



[N : NPh·OH : SO₂H = 1 : 2 : 4 and 2 : 1 : 4], the latter, however, being only obtained as its inner anhydride; they are best separated by fractional crystallisation from acetic acid.

The first compound crystallises in brownish-yellow, glistening crystals, and melts at 302–304°; it is only very sparingly soluble in water, but more readily in dilute alcohol and acetic acid. The solutions are bright yellow and exhibit a yellowish-green fluorescence. A trace of aniline colours the alcoholic solution magenta, owing to the formation of phenylrosinduline. With alkalis, it yields rosindone; with hydroxylamine and phenylhydrazine, it yields the rosindone oxime and hydrazone respectively.

The second compound, $\text{O}-\text{NPh}-\text{C}_6\text{H}_4-\text{SO}_2-\text{C}_{10}\text{H}_5-\text{N}$, crystallises in glistening, reddish-brown prisms, and melts above 360°. It is sparingly soluble in water, moderately in alcohol, and readily in 70 per cent. acetic acid. Its solutions have a reddish-yellow colour and do not fluoresce. Characteristic is its intensely sweet taste; it dissolves in sulphuric acid yielding a dirty purple-red solution. J. J. S.

Naphthazines. By OTTO FISCHER and ROB. ALBERT (*Ber.*, 1896, 29, 2086–2091; compare Fischer and Junk, *Abstr.*, 1893, i, 283).—The naphthazine (m. p. 296°) previously described is now stated to be β -naphthalido-sym.-naphthazine, $\text{C}_{10}\text{H}_7\cdot\text{NH}\cdot\text{C}_{10}\text{H}_5\llbracket\text{N}\rrbracket\text{C}_{10}\text{H}_6$, [N : N : NH = 1 : 2 : 4; N : N = 1 : 2], since, when heated with acetic and hydrochloric acids at high temperatures, it is decomposed into β -naphthylamine and a hydroxynaphthazine, which, on distillation with zinc dust, yields sym- $\alpha\beta$ -naphthazine, melting at 242° (Matthes, *Abstr.*, 1890, 993). The same naphthalidonaphthazine may also be obtained by the action of β -naphthylamine on β -amidonaphthazine. It is best purified by first washing with boiling alcohol and then crystallising from nitrobenzene. The hydrochloride, obtained by heating a xylene solution of the base with an alcoholic solution of hydrogen chloride, forms yellowish-red crystals.

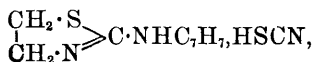
$\alpha\beta\beta$ -Naphthazine, obtained by the action of $\beta\beta$ -naphthalenediamine in cold acetic acid solution on β -naphthaquinone, crystallises in small, yellowish-brown needles. It melts at 240°, and gives a reddish-violet solution with concentrated sulphuric acid. It differs from sym-naphthazine in showing a yellowish-green fluorescence in dilute benzene solution. Its acetic acid solution is not fluorescent.

α -Amido-sym-naphthazine is obtained, together with Witt's unsym- $\alpha\beta$ -naphthazine by the elimination of water and ammonia from nitroso- β -naphthylamine and α -naphthylamine. The best yield of the sym. compound is obtained by working at as low a temperature as possible. It crystallises in light yellow needles which have a green lustre, melts at 325°, and sublimes at higher temperatures. It is practically insoluble in benzene and in alcohol, but gives a yellowish-green fluorescence to the solvents. The salts with mineral acids are red. When heated with concentrated hydrochloric acid, the sym. naphthazine is decomposed into ammonia and the hydroxynaphthazine described above. J. J. S.

Substituted Hydroxyphenyltriazoles. By GEORGE YOUNG (*Ber.*, 1896, **29**, 2311—2312).—The author points out that 3:1:5-hydroxydiphenyltriazole, recently obtained by Widman (*Abstr.*, 1896, i, 629), has been already described by him (*Trans.*, 1895, 1064). According to his observations, all aromatic substituted hydroxyphenyltriazoles, which contain no amido-group, are, contrary to the statement of Widman, insoluble in dilute acids; they dissolve in warm concentrated hydrochloric acid, and are precipitated unchanged on the addition of water. M. O. F.

Hydroxyl and Halogen Derivatives of Secondary and Tertiary Bases. By SIEGMUND GABRIEL and ROBERT STELTZNER (*Ber.*, 1896, **29**, 2381—2391).— μ -Phenyloxazoline, $\begin{array}{c} \text{CH}_2\cdot\text{O} \\ | \\ \text{CH}_2\cdot\text{N} \end{array} \gg \text{CPh}$, is readily converted by reduction with sodium and boiling amyl alcohol into *benzylhydroxyethylamine*, $\text{CH}_2\text{Ph}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OH}$, which is a thick, almost odourless oil, and boils with partial decomposition at about 280° . It dissolves readily in water, forming a strongly alkaline solution. The *aurochloride* forms pointed, rhombic tablets, melting at 105° . The *picrate* melts at 135 — 136° . The *nitrosamine* is an oil. Concentrated hydrochloric acid at 170° converts the base into *benzylchloroethylamine hydrochloride* (Goldschmiedt and Jahoda, *Abstr.*, 1891, 1351), the *platinochloride* of which melts and decomposes at 180 — 181° .

Benzylbromomethylamine crystallises in long, slender needles, melting at 190 — 191° . The corresponding *picrate* melts at 147° . When a solution of *benzylbromomethylamine hydrobromide* is distilled with an alkali, *benzylvinylamine*, $\text{C}_7\text{H}_7\cdot\text{NH}\cdot\text{C}_2\text{H}_3$, which is a colourless oil, passes over in small quantity, whilst a crystalline mass of *dibenzylpiperazine*, $\text{C}_7\text{H}_7\cdot\text{N} < \begin{array}{c} \text{C}_2\text{H}_4 \\ | \\ \text{C}_2\text{H}_4 \end{array} > \text{N}\cdot\text{C}_7\text{H}_7$, remains behind in the flask. This substance forms pointed rhombic crystals, melts at 92° , and can also be obtained by the action of benzylic chloride on piperazine; the *hydrochloride* is sparingly soluble, and crystallises in plates. *n*-Benzylethylene- ψ -thiocarbamide thiocyanate,



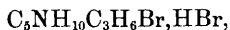
is formed by the action of potassium thiocyanate on the hydrobromide of the bromo-base; it crystallises in needles melting at 165 — 166° .

Benzylhydroxyethylamine may also be prepared by the action of benzylamine on ethylene oxide. It is then accompanied by *benzyl dihydroxydiethylamine*, $\text{CH}_2\text{Ph}\cdot\text{N}(\text{C}_2\text{H}_4\cdot\text{OH})_2$, which is a colourless oil, and boils at 225 — 225.5° (pressure = 40 mm.). It is converted by hydrobromic acid into *benzyl dibromodiethylamine hydrobromide*, which crystallises in short prisms, and melts at 191° . The free base is an oil, and the corresponding *picrate* melts at 138 — 139° . The filtrate from this bromo-base contains *benzylmorpholine hydrobromide*, which crystallises in colourless plates, melting at 234 — 235° .

The free base, *benzylmorpholine*, $\text{CH}_2\text{Ph}\cdot\text{N} < \begin{array}{c} \text{C}_2\text{H}_4 \\ | \\ \text{C}_3\text{H}_4 \end{array} > \text{O}$, is a colourless

oil, which has a faint odour of benzylamine, and boils at 260—261°. The *hydrochloride* decomposes at 244—245°, the *platinochloride* at 211°. The *picrate* melts at 184—185°, whilst the *aurochloride* melts and decomposes at 202—203°. A chloride and platinochloride of a base, probably identical with the above, have been described by Goldschmiedt and Jahoda, who, however, have given lower melting points for these compounds.

1- γ -Phenoxypropylpiperidine, $C_5NH_{10} \cdot C_3H_5 \cdot OPh$, is prepared by heating piperidine with phenylic γ -chloropropyl ether. It is an oil, which boils at 313°, and yields a crystalline *hydrochloride* and a *picrate* which melts at 113°. Attempts to displace the phenoxy-group by chlorine failed, but the compound reacts with hydrobromic acid at 100° to form 1- γ -bromopropylpiperidine hydrobromide,



which crystallises in long, flat needles, melting at 212° (compare Laun, *Ber.*, 17, 680). The *picrate* melts at 116—117°. When the base is set free and heated, only a very small amount of it distils over, the greater portion being converted into *trimethylenepiperylum bromide*, $C_5NH_{10}Br < \begin{smallmatrix} CH_2 \\ CH_2 \end{smallmatrix} > CH_2$, which is not decomposed by aqueous alkalis; it forms a very hygroscopic, crystalline mass. The *picrate* melts at 239—240°, and is obtained by the direct action of picric acid. The bromide is decomposed by silver oxide, and the hydroxide thus formed yields with hydrochloric acid and platonic chloride the *platinochloride*, which melts at 185—187°. The *aurochloride* melts at 220°. When the hydroxide is treated with an excess of hydrobromic acid, it is reconverted into the original bromopropylpiperidine hydrobromide. An excess of hydrochloric acid converts it into the corresponding 1- γ -chloropropylpiperidine hydrochloride, which crystallises in colourless scales, and melts and decomposes at 220°.

A. H.

Aromatic Oxazoles and Imidazoles. By STEPHAN S. MINOVICI (*Ber.*, 1896, 29, 2097—2106; compare this vol., i, 262.)—According to the observation of E. Fischer (*loc. cit.*), β : μ -diphenyloxazole is produced by condensation of benzaldehydecyanhydrin with benzaldehyde, and the author, applying this principle to numerous aromatic aldehydes and cyanhydrins, has found that in general, action takes place in a normal way, whilst in two cases, the compound produced by the action of the aldehyde on an amide arising from the nitrile is also formed.

β -Phenyl- μ -methoxyphenyloxazole, $N < \begin{smallmatrix} C(C_6H_4 \cdot OMe) \\ CH = CPh \end{smallmatrix} > O$, is produced when hydrogen chloride is led into an ice-cold, ethereal solution of anisaldehyde and benzaldehydecyanhydrin, the *hydrochloride* crystallising from the liquid in colourless needles or prisms, which melt and evolve hydrogen chloride at 173—174°; the base, which melts at 99°, and boils above 360°, is obtained by adding water to an alcoholic solution of the hydrochloride. The *picrate* decomposes and melts at 195°, the *sulphate* and *nitrate* melt at 225° and 116°, respectively. *Methoxybenzylidenemandelamide*, $OMe \cdot C_6H_4 \cdot CH : N \cdot CO \cdot CHPh \cdot OH$, is

deposited on evaporating the ethereal mother liquor of the foregoing substance; it melts at 182° , and, when heated at 180° with dilute alcohol, yields ammonia, anisaldehyde, and mandelic acid.

μ -Phenyl- β -methoxyphenyloxazole, $N \ll \begin{smallmatrix} \text{CPh} \cdot \text{O} \\ \text{CH} - \text{C} \cdot \text{C}_6\text{H}_4 \cdot \text{OMe} \end{smallmatrix}$, is obtained from anisaldehydecyanhydrin and benzaldehyde, methoxymandelamide being produced at the same time; it crystallises from ether in slender needles melting at $84-85^{\circ}$, and the hydrochloride evolves hydrogen chloride and melts at 195° . Benzylidenemethoxymandelamide, $\text{CHPh} \cdot \text{N} \cdot \text{CO} \cdot \text{CH}(\text{OH}) \cdot \text{C}_6\text{H}_4 \cdot \text{OMe}$, is another bye-product; it melts at 183° , and, when heated at 180° with dilute alcohol, yields ammonia and benzaldehyde, along with an acid which sublimes at 230° without undergoing fusion.

β : μ -Dimethoxydiphenyloxazole, $N \ll \begin{smallmatrix} \text{C}(\text{C}_6\text{H}_4 \cdot \text{OMe}) \\ \text{CH} : \text{C}(\text{C}_6\text{H}_4 \cdot \text{OMe}) \end{smallmatrix} > \text{O}$, is prepared from anisaldehydecyanhydrin and anisaldehyde, methoxymandelamide being also formed; it crystallises from light petroleum in prisms, and melts at 145° . The hydrochloride melts and decomposes at 195° .

β Phenyl- μ -propylphenyloxazole, $N \ll \begin{smallmatrix} \text{C}(\text{C}_6\text{H}_4 \cdot \text{Pr}) \\ \text{CH} = \text{CPh} \end{smallmatrix} > \text{O}$, obtained from cuminaldehyde and benzaldehydecyanhydrin, melts at 50° , and boils above 360° ; the hydrochloride crystallises from alcohol in prisms, and melts at 152° .

β -Methoxyphenyl- μ -propylphenyloxazole, $N \ll \begin{smallmatrix} \text{C}(\text{C}_6\text{H}_4 \cdot \text{Pr}) \\ \text{CH} : \text{C}(\text{C}_6\text{H}_4 \cdot \text{OMe}) \end{smallmatrix} > \text{O}$, is prepared from cuminaldehyde and anisaldehydecyanhydrin, and forms small needles which melt at 55° ; the hydrochloride crystallises in needles, and melts at 160° .

β : μ -Phenylstyryloxazole, $N \ll \begin{smallmatrix} \text{C}(\text{CH} : \text{CHPh}) \\ \text{CH} = \text{CPh} \end{smallmatrix} > \text{O}$, produced from cinnamaldehyde and benzaldehydecyanhydrin, crystallises from light petroleum in clusters of needles, and melts at 62° ; the hydrochloride melts at 125° .

β -Methoxyphenyl- μ -styryloxazole, $N \ll \begin{smallmatrix} \text{C}(\text{CH} : \text{CHPh}) \\ \text{C} : \text{C}(\text{C}_6\text{H}_4 \cdot \text{OMe}) \end{smallmatrix} > \text{O}$, arises from the action of cinnamaldehyde on anisaldehydecyanhydrin, and melts at $99-100^{\circ}$; the hydrochloride melts and decomposes at 175° .

β : μ -Diphenylimidazole, $N \ll \begin{smallmatrix} \text{CPh} \cdot \text{NH} \\ \text{CH} - \text{CPh} \end{smallmatrix}$, is formed when diphenyloxazole is heated at 300° with alcoholic ammonia for 6—7 hours, and crystallises from benzene in small, lustrous prisms, which melt at 162° ; the hydrochloride melts and decomposes at 273° . It is also produced by the action of hydrogen chloride on a mixture of benzaldehyde and phenylamidacetonitrile; the last-named substance, which has been hitherto known in the liquid form, crystallises from light petroleum in colourless leaflets which melt at 55° , whilst the hydrochloride crystallises from alcohol, and melts, decomposing, at 173° .

It has been shown (*loc. cit.*) that under the influence of chromic acid the oxazole ring is ruptured, and phenylglyoxylbenzamide pro-

duced; the action of chlorine is similar, the alcoholic solvent in presence of the halogen giving rise to an alkyl derivative.

Phenylglyoxylmethoxybenzylamine, $\text{OMe} \cdot \text{CHPh} \cdot \text{NH} \cdot \text{CO} \cdot \text{CPhO}$, is produced on passing chlorine into an ice-cold solution of $\beta : \mu$ -diphenyloxazole in methylic alcohol; it crystallises from the latter solvent in small needles, and melts at 105° . *Phenylglyoxylethoxybenzylamine* is obtained when ethylic alcohol is employed, and crystallises in slender needles melting at 116° . The action of the halogen on $\beta : \mu$ -diphenyloxazole dissolved in acetone, gives rise to phenylglyoxylbenzamide (*loc. cit.*).

Phenylglyoxylmethoxybenzamide, $\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{NH} \cdot \text{CO} \cdot \text{CPhO}$, is formed when chlorine is passed into a solution of β -phenyl- μ -methoxyphenyloxazole dissolved in acetone; it crystallises in slender prisms, and melts at 150° .

Nitro- $\beta : \mu$ -diphenyloxazole, $\text{C}_{15}\text{H}_{10}\text{O}_3\text{N}_2$, is obtained by the action of cold, fuming nitric acid on $\beta : \mu$ -diphenyloxazole, and crystallises from glacial acetic acid in beautiful, yellow needles, which melt at 185° ; the substance is indifferent towards alkalis and chlorine, whilst oxidation with chromic acid gives rise to paranitrobenzoic acid, and a compound, which is probably the nitro-derivative of phenylglyoxylbenzamide.
M. O. F.

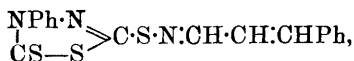
Derivatives of Hydrosulphamine. By MAX BUSCH (*Ber.*, 1896, 29, 2127—2143; compare *Abstr.*, 1894, i, 625).—

Phenyldithiobiazolone hydrosulphamine, $\begin{array}{c} \text{NPh} \cdot \text{N} \\ | \quad | \\ \text{CS} - \text{S} \end{array} \gg \text{C} \cdot \text{S} \cdot \text{NH}_2$, is obtained by the action of alcoholic ammonia on phenyldithiobiazolone bisulphide (*loc. cit.*), and crystallises from chloroform in transparent prisms; it becomes brown at 130° , and melts with effervescence at 136° . The *ammonium* derivative of phenyldithiobiazolone hydrosulphide crystallises from the mother liquor in silky needles, and melts above 200° , becoming yellow at 160° . When an alcoholic solution of the hydrosulphamine is boiled, ammonia is liberated, and the bisulphide regenerated, the same change occurring under the influence of dilute mineral acids; fusion gives rise to nitrogen and ammonia, along with phenyldithiobiazolone *tetrasulphide*, $(\text{C}_8\text{H}_2\text{N}_2\text{S}_2)_2\text{S}_4$, which crystallises from a mixture of chloroform and alcohol in small needles, and melts at 131 — 132° . Alcoholic potash readily dissolves phenyldithiobiazolone hydrosulphamine, ammonia being eliminated; on boiling the liquid, precipitation of potassium sulphite takes place, and *ethoxyphenyldithiobiazolone*, $\begin{array}{c} \text{NPh} \cdot \text{N} \\ | \quad | \\ \text{CS} - \text{S} \end{array} \gg \text{C} \cdot \text{OEt}$, crystallises out in silky needles melting at 87 — 88° when the alcoholic liquid is diluted with water.

Phenyldithiobiazolonebenzylidenesulphime, $\begin{array}{c} \text{NPh} \cdot \text{N} \\ | \quad | \\ \text{CS} - \text{S} \end{array} \gg \text{C} \cdot \text{S} \cdot \text{N} : \text{CHPh}$, is produced on heating a mixture of phenyldithiobiazolone with benzaldehyde, in molecular proportion, on the water bath; it crystallises in slender, white needles, or thick, transparent plates, and both forms melt at 154 — 155° . Alcoholic hydrochloric acid converts the sulphine into the hydrochloride of benzylideneimide (compare this vol., i, 677).

this substance being resolved into benzaldehyde and ammonium chloride under the influence of water, whilst an alcoholic solution deposits ammonium chloride, and then contains *benzylidene diethylic ether*, which melts at 180—181°, effervescing feebly.

Phenyldithiobiazolonecinnamylidenesulphime,



is prepared from phenyldithiobiazolone hydrosulphamine by heating it with cinnamaldehyde in alcoholic solution at 50—60°; it crystallises in slender, yellowish needles, and melts at 172—173°. Alcoholic hydrochloric acid converts it into *cinnamylideneimide hydrochloride*, which crystallises in lustrous needles or silvery leaflets, and is converted into a black mass at 170°; treatment with water produces ammonium chloride and cinnamaldehyde, whilst phenylhydrazine gives rise to cinnamylidenephénylhydrazone and ammonium chloride.

Phenyldithiobiazolone methylhydrosulphamine, $\begin{array}{c} \text{NPh}\cdot\text{N} \\ | \\ \text{CS}-\text{S} \end{array} \gg \text{C}\cdot\text{S}\cdot\text{NHMe}$,

obtained by the action of methylamine on phenyldithiobiazolone bisulphide, crystallises in white needles which melt at 85°; *phenyldithiobiazolone ethylhydrosulphamine* forms lustrous, white needles, and melts without decomposing at 95—96°, whilst *phenyldithiobiazolone dimethylhydrosulphamine* is a yellowish oil. The *dimethylamine* derivative of phenyldithiobiazolone hydrosulphide is produced along with the latter substance, and crystallises in lustrous leaflets melting at 117—118°; the *methylamine* derivative is associated with the methylhydrosulphamine. The *trimethylamine* derivative of phenyldithiobiazolone hydrosulphide is obtained by the action of trimethylamine on the bisulphide, and crystallises in long prisms melting at 145—146°, whilst tripropylamine gives rise to the *tripropylamine* derivative, which melts at 126°.

Phenyldithiobiazolone amidophenyl sulphide, $\begin{array}{c} \text{NPh}\cdot\text{N} \\ | \\ \text{CS}-\text{S} \end{array} \gg \text{C}\cdot\text{S}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$,

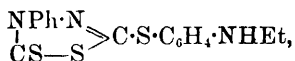
obtained by the action of aniline on phenyldithiobiazolone bisulphide, crystallises from alcohol in colourless, lustrous leaflets melting at 163—164°; the *hydrochloride* forms slender, white needles, and undergoes dissociation at 194°; the *diazo*-compound is somewhat unstable, a solution evolving nitrogen at 60—70°; and the *azo*-compound crystallises from benzene in beautiful, lustrous needles, and melts at 218°. The *aniline* derivative of phenyldithiobiazolone hydrosulphide is produced along with the amidosulphide; it is very readily soluble in alcohol, and crystallises from a mixture of this agent with ether in slender needles, melting at 155°.

Phenyldithiobiazolone phenyl sulphide, $\begin{array}{c} \text{NPh}\cdot\text{N} \\ | \\ \text{CS}-\text{S} \end{array} \gg \text{C}\cdot\text{SPh}$, is produced from the amido-derivative, by means of the diazo-reaction and crystallises from dilute alcohol in lustrous leaflets.

Phenyldithiobiazolone amidotolyl sulphide, $\begin{array}{c} \text{NPh}\cdot\text{N} \\ | \\ \text{CS}-\text{S} \end{array} \gg \text{C}\cdot\text{S}\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{NH}_2$,

is obtained from phenyldithiobiazolone bisulphide and orthotoluidine, and melts at 128° ; paratoluidine and dimethylaniline are without action on the bisulphide.

Phenyldithiobiazolone ethylamidophenyl sulphide,



is prepared from the bisulphide and ethylaniline; it crystallises from alcohol in white needles, and melts at 165° . The *nitrosamine* forms lustrous, white needles, and melts at $136-138^{\circ}$. M. O. F.

Synthesis of Dioxyazine Derivatives. By FRIEDRICH KEHRMANN and H. BÜRGIN (*Ber.*, 1896, 29, 2076—2078; compare *Abstr.*, 1894, i, 54).—Zinke and Hagen's dihydroxytoluquinone (*Abstr.*, 1883, 1118) readily reacts with orthamidophenol hydrochloride in hot, aqueous solution to form *hydroxytoluphenoxazone*; this crystallises in brown-red, prismatic crystals, melts at $215-216^{\circ}$, and dissolves in concentrated sulphuric acid. Its solutions in benzene, alcohol, and acetic acid are yellowish-red, and do not fluoresce.

Methyltriphenodioxazine, $\text{C}_6\text{H}_4 < \begin{array}{c} \text{N} \\ \text{O} \end{array} > \text{C}_6\text{HMe} < \begin{array}{c} \text{O} \\ \text{N} \end{array} > \text{C}_6\text{H}_4$, is obtained when hydroxytoluphenoxazone (1 gram) is heated with orthamidophenol hydrochloride (2 grams) and benzoic acid (20 grams) to the boiling point of the acid in a paraffin bath for one minute. When crystallised from toluene, it forms small, dark red crystals with a green, metallic lustre. Its benzene and toluene solutions are yellowish-red, and show a strong, green fluorescence. J. J. S.

Conversion of Cinchonine into Cinchonidine. By WILHELM KOENIGS and AUGUST HUSMANN (*Ber.*, 1896, 29, 2185—2187).—The authors have obtained cinchonidine by heating pure cinchonine with amyl alcoholic potash for 15—16 hours. Only about 5 per cent. of the cinchonine is thus transformed, and it has not been definitely determined whether homocinchonidine is not formed at the same time. These facts agree with the assumption that cinchonine and cinchonidine are stereoisomerides.

A considerable portion of the cinchonine, on treatment with amyl alcoholic potash, is converted into bases which are readily soluble in ether; from these a zincchloride melting at 206° was obtained.

J. J. S.

Ketones of the Tropine Group. V. An Isomeride of Cocaine. By RICHARD WILLSTÄTTER (*Ber.*, 1896, 29, 2216—2227).—From the cyanhydrin of tropinone, the ketone produced by the oxidation of tropine, a series of compounds isomeric with cocaine can be formed.

α -*Ecgonine*, $\text{C}_8\text{H}_{15}\text{NO}_3$, is formed on hydrolysing tropinonecyanhydrin with concentrated hydrochloric acid, or better, by transforming the cyanhydrin directly into the methylic salts of α -ecgonine, and subsequently hydrolysing the latter. It forms snow-white leaflets, tolerably soluble in hot water, more sparingly in cold water and in

absolute alcohol, and insoluble in ether. Its aqueous solution gives a yellow precipitate with phosphomolybdic acid, and its solution in sulphuric acid, a permanent red coloration with potassium permanganate. When recrystallised from water, α -ecgonine contains 1 mol. H_2O , but when precipitated from its aqueous solution by means of alcohol $\frac{1}{2}$ mol. H_2O ; when anhydrous, it melts and decomposes at 305° . On warming with lead peroxide and water, carbonic anhydride is immediately eliminated. The *platinochloride*, with $4\text{H}_2\text{O}$ or $5\text{H}_2\text{O}$, consists of orange-yellow cubes, readily soluble in hot water, and melting and decomposing at 223 — 224° . The *aurochloride*, with $1\text{H}_2\text{O}$, crystallises in amber-yellow prisms, readily soluble in water and alcohol, and melts and decomposes at 183 — 184° .

The *methylic salt* of α -ecgonine, $\text{C}_{10}\text{H}_{17}\text{NO}_3$, is prepared by saturating a mixture of methylic alcohol and α -ecgonine hydrochloride with hydrogen chloride; it forms colourless prisms melting at 114° , is easily soluble in water, ethylic and methylic alcohols, and in chloroform, tolerably soluble in benzene, less readily in ether, and very sparingly in light petroleum. The *hydrochloride* is readily soluble in water, and gives no precipitate with mercuric chloride; the *picrate* is tolerably soluble in hot water, but only slightly in cold water and in hot ethylic alcohol; it forms orange-yellow prisms melting at 189 — 191° ; the *platinochloride*, with $2\text{H}_2\text{O}$, melts and decomposes at 204° ; the *aurochloride* forms thin, glistening plates melting at 95 — 96° .

Methyl- α -ecgonine methiodide, $\text{C}_{10}\text{H}_{17}\text{NO}_3\text{MeI}$, is formed on adding methylic iodide to a solution of methyl- α -ecgonine in methylic alcohol. It forms glistening needles melting at 201 — 202° , is readily soluble in water and in hot acetone, almost insoluble in ethylic acetate, and, on fusion with potash, yields dimethylamine. The *aurochloride* forms golden-yellow needles melting at 120° . The *aurochloride* of α -ecgonine *methochloride* is formed on treating α -ecgonine methiodide with silver chloride; it melts and decomposes at 212° .

Benzoyl- α -ecgonine is produced on treating α -ecgonine with benzoic anhydride; it is very soluble in hot water, and often forms supersaturated solutions; it crystallises with $\frac{1}{2}$ mol. H_2O , and melts and decomposes at 209° .

α -Cocaine, $\text{C}_{17}\text{H}_{21}\text{NO}_4$, is best formed by benzoylating methyl- α -ecgonine with benzoic chloride in benzene solution; α -cocaine hydrochloride then separates as an oil, from which the artificial alkaloid is obtained by treatment with sodium carbonate, and is purified by recrystallisation from light petroleum; it forms long, transparent prisms, melts at 87 — 88° , is almost insoluble in hot and cold water, easily soluble, however, in most of the ordinary organic solvents, and has many of the properties characteristic of ordinary cocaine; it has, however, no effect physiologically. The *hydrochloride* forms needles and prisms, melts at 180° , and it is almost insoluble in water. The *hydriodide* forms glistening needles containing $1\frac{1}{2}$ mol. H_2O , and melts and decomposes at 192° . The *picrate* forms golden-yellow prisms melting at 195° ; the *aurochloride* crystallises in thin plates, melting and decomposing at 222° ; the *platinochloride* forms slender needles melting and decomposing at 220° .

α-Cocaine methiodide, $C_{17}H_{21}NO_4 \cdot MeI$, consists of cubes containing 1 mol. H_2O , soluble in most hot solvents, excepting ether, in which it is insoluble in the cold, and melts at 202° . By boiling with soda, benzoic acid is obtained.

α-Cocäthyline, $C_{18}H_{23}NO_4$, is a heavy, colourless oil. The *aurochloride* forms yellow leaves melting at 188° , and is insoluble in cold water. The *platinochloride* separates from water in anhydrous plates melting and decomposing at 215° . J. F. T.

Ketones of the Tropine Group. VI. The Action of Bromine on Tropinone. By RICHARD WILLSTÄTTER (*Ber.*, 1896, 29, 2228—2230).—Undiluted bromine reacts very energetically with tropinone, hydrogen bromide being eliminated in large quantities; the action is not so violent when the substances are dissolved in chloroform.

Tetrabromotropinone, $C_8H_5Br_4ON$, is formed by the prolonged action of bromine on tropinone hydrobromide, and is insoluble in water, concentrated hydrochloric acid, and alkalis, readily soluble in ether, benzene, acetone, and chloroform, also readily soluble in hot alcohol, ethylic acetate, and glacial acetic acid, whilst sparingly soluble in the latter solvents in the cold. It crystallises in pale yellow plates melting at 164° , and decomposing with elimination of hydrogen bromide at 190° . On oxidation with concentrated nitric acid, tetrabromotropinone yields *tribromopyridine*, $C_5NH_2Br_3$, which is purified by recrystallisation from pure nitric acid, from which it separates in long needles melting and decomposing at 167 — 168° . It is insoluble in water, readily soluble in hot alcohol, also in benzene, chloroform, ethylic acetate, and hot glacial acetic acid, but insoluble in cold hydrochloric acid and in light petroleum.

From its behaviour, on oxidation, it would appear that tetrabromotropinone has the constitution $CBr \begin{array}{c} \diagup CH_2 \text{ --- } CH_2 \diagdown \\ \text{---} CO \cdot CHBr \text{ ---} \\ \diagdown CHBr(?) \cdot NMe \diagup \end{array} CBr$.

J. F. T.

Formation of ψ -Tropigenine. By RICHARD WILSTÄTTER (*Ber.*, 1896, 29, 2231).—If there is the same relation between tropigenine (the alcoholic base formed by the oxidation of tropine) and ψ -tropigenine (the isomeric compound produced by the oxidation and subsequent reduction of tropigenine), as between tropine and Liebermann's ψ -tropine, then ψ -tropigenine should be directly formed from ψ -tropine on oxidation.

By oxidising ψ -tropine, dissolved in aqueous potash, with potassium permanganate, ψ -tropigenine is undoubtedly produced, and can be identified by means of its carbamate melting at 140° , its orange-yellow aurochloride, melting and decomposing at 212° ; and, finally, by means of its *n*-benzoyl derivative (m. p. 166°), prepared by Schotten's method. J. F. T.

Chemistry of the Cactaceæ. By ERVIN E. EWELL (*J. Amer. Chem. Soc.*, 1896, 18, 624—643).—A summary of Lewin and of VOL. LXX. i.

Heffter's work on the alkaloids derived from the various species of *Anhalonium* (compare Abstr., 1895, i, 120; this vol., i, 194, 267). The author has isolated two other alkaloids from mescal buttons (*Anhalonium Lewinii*), one of which is more physiologically active than those previously obtained from these cacti. Details will be published later. J. F. T.

Bebeerine or Bebirine. By MAX SCHOLTZ (*Ber.*, 1896, **29**, 2054—2058).—Bebirine is readily obtained in an amorphous condition from commercial "bebeerinum purum" by extraction with ether. The yellow powder thus procured dissolves readily in methylic alcohol, but soon begins to separate rapidly and finally forms a pulp composed of small, colourless, shining prisms. The crystalline compound, on analysis, gave numbers in agreement with the formula, $C_{18}H_{21}NO_3$, given by Bodeker (*Annalen*, 1849, **69**, 54) and Flückiger (*N. Jahrb. Pharm.*, **31**, 257). When crystalline, it melts at 214° , and dissolves sparingly in alcohol, but after dissolution in acetone or chloroform separates in the amorphous condition and has the melting point, 180° , and other properties of that modification; it dissolves in hydrochloric acid, and the solution, on evaporation, deposits the *hydrochloride* in the form of bundles of small needles melting at 259 — 260° .

The behaviour of the substance towards nitrous acid proves that the base is a tertiary amine; when it is heated with methylic iodide, the *methiodide*, $C_{18}H_{21}NO_3 \cdot MeI$, is produced; this crystallises in slender, silky needles, and melts at 268 — 270° .

Bebirine contains no methoxy- or ethoxy-groups, but it dissolves in soda, thus evincing a phenolic character, which is further indicated by the behaviour of the base towards acidic anhydrides; when heated gently with acetic anhydride, a *monacetyl* derivative, $C_{18}H_{20}NO_3 \cdot Ac$, is obtained; this melts at 147 — 148° , and is insoluble in soda, but dissolves readily in acids. The *benzoyl* derivative, $C_{18}H_{19}NO_3 \cdot Bz$, prepared in a similar manner, melts at 139 — 140° . No aldehydic or ketonic group is present in bebirine.

The base is oxidised if left in contact with alkaline ferricyanide during six hours, and then, the addition of ammonium chloride causes a precipitate of a basic substance, $C_{18}H_{19}NO_4$; the latter is sparingly soluble in alcohol, and chars when heated above 260° .

The alkaloid is optically active, a 1.6 per cent. solution in alcohol having a rotation $[\alpha]_D = -298$. A. L.

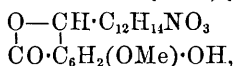
Cuskygrine. By CARL T. LIEBERMANN and GUSTAV CYBULSKI (*Ber.*, 1896, **29**, 2050—2051; compare Abstr., 1895, i, 310).—The author's statement that cuskygrine affords little or no hygric acid on oxidation with chromic acid, is now proved to be erroneous; under altered conditions, a fairly good yield of the acid is obtained together with an oily substance, possibly a second acid, which gradually assumes a crystalline form, but is hygroscopic and difficult to purify.

The production of hygric acid from cuskygrine is indicative of its derivation from a methylpyrrolidine. A. L.

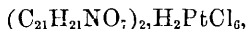
Derivatives of Isonarcotine. By CARL T. LIEBERMANN (*Ber.*, 1896, 29, 2040—2045; compare this vol., i, 264).—*Bromisonarcotine*, $\text{O}-\text{CH}\cdot\text{C}_{12}\text{H}_{13}\text{NO}_3$
 $\text{CO}\cdot\text{C}_6\text{HBr}(\text{OMe})_2$, is obtained when 3 parts of bromopianic acid and 2 parts of hydrocotarnine are treated with sulphuric acid in a manner similar to that described in the first paper (*loc. cit.*). The base dissolves readily in alcohol, and crystallises therefrom on the cautious addition of water; it melts at 175° . Its hydrochloride and sulphate are sparingly soluble in cold water; unlike isonarcotine, when dissolved in sulphuric acid it gives only a feeble yellow coloration; its double salts with gold and platinum are obtained as flocculent, yellow precipitates. In order to ascertain whether it was derived from narcotine or isonarcotine, it was reduced with zinc dust and hydrochloric acid, and the base formed was liberated with ammonia the substance thus obtained had all the properties of isonarcotine.

Nitroisonarcotine, $\text{O}-\text{CH}\cdot\text{C}_{12}\text{H}_{14}\text{NO}_3$
 $\text{CO}\cdot\text{C}_6\text{H}(\text{OMe})_2\cdot\text{NO}_2$, prepared from nitropianic acid and hydrocotarnine, crystallises from dilute alcohol in yellow needles, and melts and decomposes at about 205° . It dissolves readily in hydrochloric acid, and its solution in sulphuric acid is yellow.

Methylnorisonarcotine, $\text{COOH}\cdot\text{C}_6\text{H}_2(\text{OMe})(\text{OH})\cdot\text{CH}\cdot\text{C}_{12}\text{H}_{13}\text{NO}_3$, or



prepared from methylnoropianic acid and hydrocotarnine, is precipitated from its solution in dilute sulphuric acid, on adding excess of soda, as a sodium salt, from which the hydrochloride of the base may be obtained by means of hydrochloric acid. The free base dissolves sparingly in water, imparting to it a weak alkaline reaction; it is somewhat readily soluble in alcohol, and is deposited from hot benzene in crystals containing $\frac{1}{2}$ mol. benzene of crystallisation, the greater portion of which is lost, in a desiccator over paraffin, in about 12 days. It melts and decomposes at 209° , whilst the freshly prepared benzene compound melts at $149-151^\circ$. It dissolves in concentrated sulphuric acid with the same red coloration as is observed in the case of isonarcotine, and its alcoholic solutions, with ferric chloride, give the beautiful blue coloration characteristic of hydroxy-compounds. The *sodium* salt of methylnorisonarcotine is insoluble in alcohol, but crystallises from boiling amyl alcohol. A solution of the base in dilute ammonia gives white precipitates of the calcium and silver salts on the addition of calcium chloride and silver nitrate respectively. The *hydrochloride*, *nitrate*, *sulphate*, and *picrate* of methylnorisonarcotine are all sparingly soluble in cold water, the first crystallising in small, white leaflets; the platinochloride,



is obtained as a yellow precipitate.

The production of the above compounds has induced the author to investigate the behaviour of aldehydes in general towards hydrocotarnine; benzaldehyde unites with the latter to form *hydroxy-benzylhydrocotarnine*, $\text{OH}\cdot\text{CHPh}\cdot\text{C}_{12}\text{H}_{14}\text{NO}_3$; this crystallises from

dilute alcohol, melts and decomposes at about 240° , and dissolves in sulphuric acid with the production of a feeble yellow coloration; it has a feeble alkaline reaction, yields a deliquescent hydrochloride, and an amorphous platinochloride and aurochloride; it is not affected by phosphorus oxychloride. Cinnamaldehyde reacts with hydrocotarnine in a similar manner. A. L.

Scopolamine. By ERNST SCHMIDT (*Ber.*, 1896, **29**, 2009—2014; compare Abstr., 1895, i, 158).—Replying to the criticism of Hesse (this vol., i, 655), the author points out that the substance described by Hesse as atroscine closely resembles the inactive scopolamine, which he has previously described, and which is formed by the action of alkalis on scopolamine hydrobromide. He proposes to institute a careful comparison of the two in order to decide the question. The inactive scopolamine has precisely the same physiological action as the active modification. A. H.

Occurrence of Stachydrine in the Leaves of *Citrus vulgaris*. By ERNST JAHNS (*Ber.*, 1896, **29**, 2065—2068).—The chief basic constituent of leaves of the bitter orange (*Citrus vulgaris*) is stachydrine, which has already been obtained from the tubers of *Stachys tuberosa* (compare von Planta and Schulze, Abstr., 1893, i, 447, 679). The free base crystallises with $1\text{H}_2\text{O}$, which it loses at 100° . Its *methylic salt*, $\text{C}_7\text{H}_{12}\text{MeNO}_2$, is obtained in the form of its *hydrochloride*, on saturating a methylic alcoholic solution of the base with hydrogen chloride and evaporating at the ordinary temperature. The *free ether* is readily decomposed; its *aurochloride* forms glistening plates, melts at 85° , and is more sparingly soluble than stachydrine aurochloride.

Stachydrine, when boiled with concentrated potash solution, yields dimethylamine, and its general properties agree with the formula $\text{NMe}_2\cdot\text{C}_6\text{H}_6\cdot\text{COOH}$. J. J. S.

Urobilin. By ARCHIBALD E. GARROD and F. GOWLAND HOPKINS (*J. Physiol.*, 1896, **20**, 112—143).—With the exception of Jaffe's method, which is difficult of application, the processes usually employed for the extraction of urobilin from urine are not calculated to yield a pure product. The method used in the present experiments consists in precipitating the pigment by saturating the urine with ammonium sulphate after it had been previously saturated with ammonium chloride to free it from urates. The pigment is then dissolved out from the precipitate by water, and reprecipitated with ammonium sulphate, this process being repeated several times; the final precipitate is dissolved in dilute ammonia, precipitated with a minimal excess of sulphuric acid, washed with saturated solution of ammonium sulphate, and freed from this salt by solution and re-solution in absolute alcohol.

Another method used is to remove the urates by ammonium chloride, acidify with sulphuric acid, and saturate with ammonium sulphate. The urine so treated, yields its urobilin readily to solvents, of which a mixture of chloroform and ether (1 : 2) is recommended as the most selective; the ether-chloroform extract is then shaken

with water to which a trace of alkali has been added, the pigment passing into solution in the alkaline water. This solution is once more saturated with ammonium sulphate, and the process of extraction with ether-chloroform repeated.

Urobilin, obtained from various human sources, that is, from normal and morbid urines, from fæces and from bile, is one and the same substance. Specimens from these several sources have, when pure, identical chemical and optical properties, and show in common a spectroscopic character which has not been previously described, namely, a second, narrow absorption band in the neighbourhood of the E line when the pigment is partially precipitated from an aqueous alkaline solution by acidification. The differences which have been described as existing between the different products are in part due to impurities in the specimens examined, and in part to the varying amounts of urobilin in the specimens. Urobilin is an unstable substance, and is liable to undergo certain modifications; these modified pigments have not the properties of the described pathological urobilins, and are capable of reversion into the typical form. W. D. H.

Absorption of the extreme Violet and Ultra-violet Rays of the Solar Spectrum by Hæmoglobin, its Compounds, and certain of its Derivatives. By ARTHUR GAMGEE (*Proc. Roy. Soc.*, 1896, 59, 276—279).—Compounds of hæmoglobin with oxygen, carbonic oxide, and nitric oxide present, even in highly dilute solutions, an absorption band between Fraunhofer's lines G and H. In the case of oxyhæmoglobin, the mean ray absorbed coincides with λ 414.0.

The absorption band of the compound of carbonic oxide with hæmoglobin is slightly displaced towards the less refrangible end of the spectrum, and the compound with nitric oxide behaves identically, the mean ray absorbed being λ 420.5.

By reduction, or by boiling in a vacuum, the molecule of dissociable oxygen is removed from oxyhæmoglobin, and the absorption then corresponds with λ 426.0.

The absorption of the extreme violet depends on the iron-containing moiety of the hæmoglobin molecule.

Very dilute alkaline solutions of hæmatin exert a general absorption of the ultra-violet and extreme violet, but present no trace of definite absorption.

The acid compounds of hæmatin exhibit an absorption band which is exactly on the boundary of the ultra-violet proper, and which extends further into the ultra-violet as the concentration of the solution increases.

Solutions of hæmochromogen (Stokes' reduced hæmatin) exhibit an intense absorption band between h and G in the same position as the CO-hæmoglobin band, but more intense, the mean's ray corresponds with λ 420.0.

The absorption of the extreme and ultra-violet by methæmoglobin indicates that the substance is the product of a partial decomposition of the oxyhæmoglobin molecule.

The band in the extreme violet (and ultra-violet), which is characteristic of hæmoglobin, in no respect depends on the iron in the molecule.

This conclusion is based; (1) on the fact that none of the compounds of iron have the properties of producing a definite absorption in the extreme violet, or the adjacent ultra-violet; (2) on the study of hæmatoporphyrin, a substance derived from hæmatin by the removal of the iron.

Acid solutions of hæmatoporphyrin of extreme dilution exhibit an absorption band between h and H . If the solution be slightly more concentrated, K is absorbed, and the absorption of the ultra-violet extends more and more with concentration. Alkaline solutions of hæmatoporphyrin absorb the same spectral region, but with greater intensity.

Neither bilirubin, hydrobilirubin, nor urobilin present any definite absorption band in the region of the spectrum in which the absorption bands of hæmoglobin and its derivatives occur. J. F. T.

Relations of Turacin and Turacoporphyrin to the Colouring Matter of the Blood. By ARTHUR GAMGEE (*Proc. Roy. Soc.*, 1896, **59**, 339—342).—Solutions of turacin in caustic soda or ammonia so dilute as to be almost colourless, absorb the extreme violet and ultra-violet rays of the spectrum in precisely the same way as highly diluted solutions of the acid compounds of hæmatin, the resemblance being so complete that it is impossible to distinguish from the photographs of the spectrum which substance has been employed (compare preceding abstract).

Turacoporphyrin, formed by the action of strong sulphuric acid on turacin, presents in the ultra-violet an intense absorption band identical with that of hæmatoporphyrin obtained by the action of concentrated sulphuric acid on pure hæmatin.

These facts point to the essential identity of turacoporphyrin and hæmatoporphyrin, and, when taken in connection with the identity of the ultra-violet spectrum of turacin and of the acid hæmatin compounds, seems to show that turacin contains the atomic group which is the cause of the extreme violet and ultra-violet absorption spectra exerted by hæmoglobin, its compounds and principal derivatives.

J. F. T.

The Proteïds of Malt. By THOMAS B. OSBORNE and GEORGE F. CAMPBELL (*J. Amer. Chem. Soc.*, 1896, **18**, 542—558).—On the extraction of malt with water, five distinct substances are produced, namely, a globulin, an albumin, and three proteoses. *Bynedestin* (malt globulin) is readily soluble in dilute salt solution, from which it is precipitated on the addition of water. This globulin contains 2 per cent. more carbon and 3 per cent. less nitrogen than edestin.

Leucosin is identical in composition and properties with that found in wheat, rye, and barley (this vol., i, 399, 455); it is intimately associated with diastase, and is partially precipitated from its solutions on saturation with sodium chloride or magnesium sulphate.

A *protoproteose* readily precipitated from its aqueous solution by alcohol, and a *protoproteose* less readily precipitated, were also obtained; the composition of the former is the same as that of leucosin, that of the latter is, however, different. The presence of a deutero-proteose and a heteroproteose was also detected.

Brynin is a proteid soluble in water and in saline solutions; it forms about 1.25 per cent. of the malt.

A *proteid*, insoluble in water, in salt solution, and in alcohol, was also isolated. The composition and properties of this proteid were not determined. J. F. T.

The Proteids of the Potato. By THOMAS B. OSBORNE and GEORGE F. CAMPBELL (*J. Amer. Chem. Soc.*, 1896, **18**, 575—582).—The proteids of the potato consist of a globulin for which the name *tuberin* is proposed, and a proteose, the latter, however, occurring only in small amounts.

Tuberin is precipitated by saturating its solutions with sodium chloride, sodium sulphate, magnesium sulphate or ammonium sulphate. With acetic or nitric acids, a precipitate is given readily soluble in an excess of acid. Potassium ferrocyanide, and mercuric chloride, give no precipitate, but picric acid or tannic acid throw down the globulin. With the biuret, Millon's, and the xanthoproteic tests, the usual reactions are given. Tuberin is soluble in very dilute saline solutions; when dissolved in a 10 per cent. sodium chloride solution it shows a somewhat variable heat-coagulation point, depending on the conditions under which it is tested; but in general a flocculent coagulum is formed on heating to 60—65°. Coagulation is, however, not complete until the solutions have been heated for some time at 80°.

J. F. T.

Legumin and other Proteids of the Pea and the Vetch. By THOMAS B. OSBORNE and GEORGE F. CAMPBELL (*J. Amer. Chem. Soc.*, 1896, **18**, 583—609).—Peas and vetches contain the same proteids, which are nearly, if not entirely soluble in 10 per cent. sodium chloride solution. The greater part of the proteids consists of a globulin, Braconnot's legumin, which is readily precipitated on dialysing its salt solutions; with nitric acid, Millon's and Ademkiewicz's reagents, it gives the usual proteid reactions. With strong solutions of legumin, the biuret test gives a violet colour at first, which, on standing, becomes crimson-red, similar to the colour produced by peptones.

The legumin from the vetch is not coagulated by heat, nor even rendered turbid by prolonged boiling of its strong solution. The legumin from the pea, however, is partly coagulated by heating strong solutions in a water bath and sets to a firm jelly after thus heating for some time, this being the only essential difference between them. Besides the legumin, the pea and the vetch contain another proteid in small amount, either an albumin or a globulin, which is soluble in extremely dilute salt solutions; the solutions being coagulated when heated to 80°.

Further, a very little proteose is present in the extracts of both seeds.

J. F. T.

Conglutin and Vitellin. By THOMAS B. OSBORNE and GEORGE F. CAMPBELL (*J. Amer. Chem. Soc.*, 1896, **18**, 609—623).—The proteid present in the almond and the peach-kernel is amandin and not conglutin or vitellin, which are the names usually associated with this substance.

Amandin is readily soluble in very dilute acetic acid, and is dissolved in hydrochloric acid with the development of a violet-blue coloration on standing; with the biuret test, and also with a mixture of glacial acetic acid and concentrated sulphuric acid, solutions of this globulin give a fine violet colour.

Corylin is the proteid of the walnut (*Juglans regia*), and hazel nut. When dry, it is a heavy, snow-white powder which is quite insoluble in distilled water at 20° or at 40°; it is, however, readily soluble in a 10 per cent. solution of sodium chloride. With the biuret test, the usual violet colour is obtained; and with Millon's and the xantho-protein tests, the ordinary proteid reactions ensue. When dissolved in concentrated hydrochloric acid, a violet-blue coloration develops on standing; with glacial acetic acid and concentrated sulphuric acid, solutions of corylin give a violet colour.

To the proteids from the Brazil-nut (*Bertholletia excelsa*), and the oat-kernel are given the names *excelsin* and *avenalin* respectively.

Hemp (*Cannabis sativa*), squash (*Cucurbita maxima*), and castor bean (*Ricinus communis*), contain edestin.

Lupin (*Lupinus*) contains, as the principal proteid, conglutin.

The sun flower (*Helianthus*) contains edestin, contaminated with Ludwig and Kromayer's helianthotannic acid. J. F. T.

Leucinimide, a product of Hydrolysis of Proteids with Boiling Acids. By C. HEINRICH L. RITTHAUSEN (*Ber.*, 1896, 29, 2109—2110).—In a work on the proteids of grain, published in 1872, the author described leucinimide, $C_5H_{11}NO$, as occurring in the residue from the preparation of tyrosine, leucine, glutamic acid, and aspartic acid, obtaining it in woolly masses of needles. This substance is now shown to be identical with the pyridine derivative, C_5H_7NO , obtained by Cohn, on hydrolysing albumin with boiling hydrochloric acid (this vol., i, 658). M. O. F.

Chemical Nature of Diastase. II. By THOMAS B. OSBORNE and GEORGE F. CAMPBELL (*J. Amer. Chem. Soc.*, 18, 536—542; compare this vol., i, 398).—Finely ground malt was treated with a solution of sodium chloride, and the filtrate saturated with ammonium sulphate; after filtration, the liquid was subjected to repeated dialysis into alcohol (0.86 sp. gr.). By this means, several fractions were obtained, which, after being further dialysed into water and then into alcohol, were dehydrated with absolute alcohol, and dried over sulphuric acid. The two middle fractions were found to be the most active, giving a diastatic power corresponding to 300. Only a small quantity of diastase was precipitated by bringing the alcohol-content of the malt extract to 50 per cent.

The purer the diastase is made, the more sensible it is to external conditions, and the method of testing the purity of the ferment by its maltose-producing power thus becomes of uncertain value. It is possible to roughly judge of the diastatic power of a preparation by heating a portion of its solution to 65°, and observing the amount of coagulate formed. J. F. T.

JOURNAL

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ABSTRACTS OF CHEMICAL PAPERS PUBLISHED IN
BRITISH AND FOREIGN JOURNALS.

PART II.

General and Physical Chemistry.

Spectrum of Helium. By WILLIAM CROOKES (*Chem. News*, 1895, 72, 87—89).—Helium from different sources was examined spectroscopically. Five samples of gas came under investigation: (1) from clèveite, (2) from the uraninite of Hillebrand, (3) from Bröggerite, (4) from Bröggerite by fractional distillation, (5) "Helium Purissimum," gas obtained by Ramsay from various sources and purified to the highest possible point. The gas was sealed in tubes and exhausted to the most luminous point for spectroscopic examination. In most cases, no internal electrodes were employed, but metallic terminals were attached to the outside of the tube. The wave-lengths observed are given on Rowland's scale, and lines in the spectra of mercury, cadmium, zinc, and tin were used for reference. Tables are given of the wave-lengths of lines which appear to be special to the gas from uraninite, to all samples of the gas, and lines probably identical with those of the chromosphere and prominences. H. C.

The Constituents of the Gas from Clèveite. By CARL RUNGE and F. PASCHEN (*Phil. Mag.*, 1895, [2], 40, 297—302).—The authors have carefully mapped and recorded all the lines found in the spectrum of the gas from Clèveite, the bolometer being employed for the infra-red rays. Six series of lines are obtained, which the authors consider are divisible into two systems. Of these series, it is noticeable that two consist of double lines with equal differences of oscillation frequency. The spectrum also shows considerable analogy to those of the alkalis, as is seen by the comparison of the diagrams of hydrogen, clèveite gas, and lithium spectra. It further appears

from this comparison that the helium series (the series containing the D_3 line) corresponds with the constituent of higher atomic weight, a result confirmed by the observation that when the gas is allowed to stream into an exhausted Geissler tube through an asbestos plug, the helium series does not reach its maximum of brightness as quickly as the other series. The authors assign the atomic weight of 5 and 3 as probable for the two constituents. L. M. J.

Argon and its Fluorescence Spectrum. By E. DORN and HUGO ERDMANN (*Annalen*, 1895, **287**, 230—232; compare Abstr., 1895, ii, 337).—The authors criticise Berthelot's examination of the fluorescence spectrum of argon, obtained on submitting a mixture of benzene vapour with the gas to the action of the silent discharge (*loc. cit.*). They maintain that the brilliant yellow line at about $\lambda 579$, and the green line at about $\lambda 547$, have the appearance of double lines; they point out that these lines coincide with prominent bands of the mercury spectrum, and attribute the brilliant violet band at about $\lambda 438$ to the same source, the violet band at about $\lambda 436$ being probably due to nitrogen. M. O. F.

Blue Spectrum of Argon. By HEINRICH KAYSER (*Chem. News*, 1895, **72**, 99—100).—A preliminary list of the wave-lengths of the lines of the blue argon spectrum between $\lambda = 340 \mu\mu$ and $\lambda = 520 \mu\mu$ is given. The lines of the blue argon spectrum do not appear among the Fraunhofer lines, as appears from a comparison with Rowland's publications on the lines of the solar spectrum. H. C.

Spectrum of Ramsay's Compound of Argon and Carbon. By WILLIAM CROOKES (*Chem. News*, 1895, **72**, 99).—The compound of argon and carbon formed by an electric arc between purified carbon poles in an atmosphere of argon (this vol., ii, 20) has been submitted to spectroscopical examination. No lines other than those of the argon, carbon, or water vapour spectra were observed, the spectrum of water vapour being due to the gas not having been perfectly dried before it was sealed in the tube. The compound of argon and carbon gives a channelled band-spectrum similar to that of most carbon compounds. H. C.

Different Spectra of Mercury. By JOSEPH M. EDER and A. VALENTA (*Ann. Phys. Chem.*, 1895, [2], **55**, 479—502).—The authors have examined the behaviour of the mercury spectrum at different temperatures and under different conditions of pressure, studying the spark and arc spectrum and the spectrum of mercury in vacuum tubes. They have in this way extended the data for the line spectrum and have discovered a new band spectrum of mercury, to which special interest attaches as mercury vapour is thus shown to be analogous to other gases, such as hydrogen and nitrogen, for which also line and band spectra have been observed. This band spectrum appears only under certain definite conditions, namely, when the spark of a powerful induction coil (without Leyden jar) is passed through a vacuum tube in which a drop of mercury is kept at the boiling point and is therefore being distilled. A description and

measurements of the principal lines in the two mercury spectra are given in the paper. The occurrence of the two spectra in the case of mercury is of peculiar interest, as in other instances the band spectra have been attributed to molecules composed of several atoms and the line spectra to the atoms themselves. This explanation will obviously not hold in the case of mercury, the molecule of which is known to be monatomic.

H. C.

Transferring Gases to Vacuum Tubes for Spectroscopic Examination. By JAMES YOUNG and CHARLES R. DARLING (*Chem. News*, 1895, 72, 39).—The vacuum tube is fused to one arm of a T-piece of capillary glass tubing fitted with a three-way cock at the junction, another arm connects with a vacuum pump, and the third arm, by means of a mercury joint, with the gas in a tube over mercury; the gas tube has an ordinary stopcock at the top. The operations to be followed are exhausting the vacuum tube, exhausting the tube space between the stopcocks, washing the vacuum tube by admitting some of the gas three times successively, exhausting between each, and then finally charging the tube, which may be examined while attached to the system or may be sealed off and examined subsequently.

D. A. L.

Action of the Infra-red Rays on Silver Sulphide. By H. RIGOLLOT (*Compt. rend.*, 1895, 121, 164—166).—Two plates of silver, sulphurised by electrolysing a solution of sodium sulphide with a weak current for a short time, and placed in a dilute saline solution, constitute an electrochemical actinometer. With plates, 40 mm. long and 2 mm. broad, the effect of the infra-red rays of the solar spectrum can be traced to a considerable distance below the visible red, and the minima at 96 and 116, and the maximum at about 104, observed by Langley, can be recognised. The maximum electromotive force developed is 0.003 to 0.004 of a volt. In the visible spectrum, the effect decreases rapidly from A to F, and then becomes negligible.

By arranging the two plates in a U-tube, one limb of which can be heated, it is found that a difference of 6° to 7° is necessary to produce an E.M.F. of 0.002 volt. Moreover, the illuminated plate is always negative to the other, whatever the nature of the saline solution, whilst the heated plate is negative to the cold plate in solutions of silver salts, but positive in solutions of all other salts. It follows, that the effect of the infra-red rays cannot be attributed solely to an increase in the temperature of the illuminated plate.

C. H. B.

The Clark Cell when Producing a Current. By SIDNEY SKINNER (*Phil. Mag.*, 1895, [5], 39, 375—376).—A reply to some criticisms of Threlfall on the author's previous paper (*Abstr.*, 1895, ii, 34).

L. M. J.

The Tin Chromic Chloride Cell. By SIDNEY SKINNER (*Phil. Mag.*, 1895, [5], 39, 444—447).—A cell is formed, in which one electrode is a tin amalgam at the bottom of a test tube, the other a platinum plate, and the electrolyte is a solution of green chromic chloride. The action of this compound on tin is a reversible one,

$\text{Cr}_2\text{Cl}_6 + \text{Sn} \rightleftharpoons \text{SnCl}_2 + 2\text{CrCl}_2$, the direct action occurring at high temperature. The author shows that the E.M.F. is not zero at ordinary temperatures, as stated by Case, but is about 0.44 to 0.52 volt, and alters only very slightly when heated to 100° . The cell polarises, however, so rapidly at low temperatures, that at the moment of connection the effective E.M.F. is almost zero, which is the probable cause of Case's results.

L. M. J.

New Form of Battery. By MORISOT (*Compt. rend.*, 1895, 121, 251—253).—The outer cell contains a plate of gas carbon immersed in a mixture of 1 volume of sulphuric acid with 3 volumes of a cold saturated solution of potassium dichromate; the inner cell contains an amalgamated zinc plate in a concentrated, aqueous solution of sodium hydroxide, and there is an intermediate porous cell containing a solution of sodium hydroxide of sp. gr. about 1.05. The object of this intermediate cell is to retard the formation of normal chromate in the outer cell, and of zinc hydroxide round the zinc plate.

The E.M.F. of the cell is 2.5 volts at first, provided the porous cells have become thoroughly impregnated with liquid before the circuit is closed, and remains higher than 2.4 volts even after 10 hours uninterrupted action.

The substitution of a concentrated solution of sodium hydroxide for the dilute acid in a Bunsen cell, has the same effect on the E.M.F., and increases it by 0.4 volt. The zinc is less readily attacked by the alkali solution than by the ordinary dilute acid, but the expenditure of zinc is partly replaced by expenditure of alkali, and if carbon is substituted for zinc in the inner cell, there is at first an E.M.F. of 1 volt. If the zinc were attacked to the same extent as in the Poggendorff cell, there should be an E.M.F. of 3.1 volts. After some time, the zinc acquires a grey coating, which is rapidly removed by immersing it in dilute acid. The dilute alkali solution in the intermediate cell should be renewed from time to time. No advantage is gained by using potassium hydroxide in place of sodium hydroxide, or sodium dichromate in place of the potassium salt.

C. H. B.

Thermodynamics of Galvanic Polarisation. By MAX LE BLANC (*Zeit. physikal. Chem.*, 1895, 17, 740—742).—A reply to some criticisms of Jahn and Schönrock (*Abstr.*, 1895, ii, 198).

L. M. J.

Thermo-electric Powers of Metals and Alloys. By JAMES DEWAR and JOHN A. FLEMING (*Phil. Mag.*, 1895, [5], 40, 95—119).—The investigations of Tait indicated that in many cases the thermo-electric lines ($d \text{ E.M.F.}/dt$, ordinates; T abscissæ) should be straight lines, so that the curves representing thermo-electromotive force as a function of the temperature should be parabolas. The authors have, therefore, determined the thermo-electromotive force at temperatures as low as the boiling point of liquid air; the couples were in all cases prepared by the junction of the metal wire, "M," with a lead wire, and the observations were afterwards reduced to those of a couple of "M" with pure lead. Measurements were taken at about 30 temperatures between 100° and -200° (the temperature being determined

by a platinum resistance thermometer, and recorded in "platinum degrees"), and very careful measurements were taken at fixed temperatures, that is, the boiling point of oxygen, melting point of solid carbonic anhydride, &c. The metals examined were platinum, gold, palladium, silver, copper, zinc, cadmium, magnesium, tin, iron, nickel, steel, manganese-steel, manganin, German silver, platinoid, bismuth (A, B, and C), antimony and aluminium, and also carbon. The lines (E.M.F. against T) are in all cases curved, with frequently a maximum, but none are exact parabolas. Some have changes of curvature, so that the lines of thermo-electric power would be broken, whilst it is noticeable that antimony has two neutral points, and all specimens of bismuth exhibit a sudden break at about -80° pt. The authors, however, postpone the complete discussion of the curves and their interpretation.

L. M. J.

Electric Resistance of Bismuth at Low Temperatures. By JAMES DEWAR and JOHN A. FLEMING (*Phil. Mag.*, 1895, [5], 40, 303—311).—The resistance was determined in the case of three samples of bismuth; 1, commercial pure bismuth (A); 2, and 3, pure samples specially prepared (Band C), the temperature varying from 95° to -235° (platinum degrees). In each case the specific resistance at first diminishes, a minimum being reached at -50° pt. (B); -83° pt. (C), and 0° (A); after this the resistance increased, the temperature coefficient being negative. In the case of the commercial bismuth (A), a maximum was reached at about -200° pt., after which the temperature coefficient was again positive; but in the two pure samples no such maximum occurred neither was there any indication that a maximum would be reached. It is noticeable that the change in the temperature coefficient of the pure bismuth (especially C), occurs at about the same temperature as that of the discontinuity in the thermoelectric power (see preceding abstract). It is also found that the effect of a magnetic field on the resistance of the metal is very much increased by reduction of temperature; an increase of 5 per cent. due to a magnetic field reaching 25 per cent. at the temperature of liquid air.

L. M. J.

Electrical Conductivity and Dissociation Tension of Palladium Hydride. By ALEXANDER KRAKAU (*Zeit. physikal. Chem.*, 1895, 17, 689—704).—Considering previous determinations unsatisfactory, the author redetermined the conductivity of the palladium hydrogen alloy, with varying hydrogen content, and also the dissociation tension. The exact quantitative determinations are not recorded, but the author gives as general results that the resistance increases proportionally to the hydrogen until the latter reaches 30 vols., when the rate of increase diminishes gradually until the hydrogen content is 50 vols., after which it is again proportional to the occluded hydrogen. The dissociation tension gave a very similar curve, being proportional to the hydrogen until the latter reaches 40 vols., when the curve bends and becomes almost parallel to the hydrogen axis, and the influence of temperature on the point where this occurs is very slight. The author considers that the results indicate

that the hydrogen is at first dissolved in the metal and afterwards when the quantity has reached a required limit, commences to form the compound Pd_2H . L. M. J.

Note by Abstractor.—No mention is made of the researches of Hoitsema (Abstr. 1895, ii, 383), who obtained a curve apparently similar to that of the author, but who considered that the curves were not compatible with the formation of a compound Pd_2H .

Influence of Pressure on the Electrical Conductivity of Solutions. By GUSTAV TAMMANN (*Zeit. physikal. Chem.*, 1895, 17, 725—736).—The influence of pressure on conductivity may be divided into three factors; (1) volume alteration; (2) alteration of viscosity and ion friction; (3) alteration of the degree of dissociation. The effect of pressure on viscosity has been determined by Cohen (*Ann. Phys. Chem.*, 1892, [2], 45, 666), for sodium chloride solutions, the viscosity of solutions of small internal pressure diminishes with increase of pressure, the reverse obtaining with solutions of high internal pressure. The effect on the dissociation constant is given in a table of percentage alteration due to pressure of 500 atmospheres for solutions of varying concentration and dissociation. The total effect is then considered and typical curves are given. At infinite dilution, factors 1 and 2 alone are weighty and these cause an increase of about 4.5 per cent. (for 500 atmos.). If the concentration increases, there are three types of curves; (I) where the electrolyte is feebly dissociated, the curve rises to a maximum and slowly falls; (II) where the dissociation is great and factor 3 of small account, the curve is at first almost parallel to the axis of concentration, then slowly sinks owing to the effect of the viscosity, and finally cuts the axis; (III) for intermediate dissociation, the rise is not as rapid as in (I), and a well marked maximum occurs. The curve is also given in the case of sulphuric acid, which is shortly considered; a maximum occurs here at concentration 0.5 per cent. and a minimum at 85 per cent. L. M. J.

Complex Tartrates and Alkaline Solutions of Copper and Lead. By LOUIS KAHLENBERG (*Zeit. physikal. Chem.*, 1895, 17, 577—619).—The lead potassium and copper potassium double tartrates are first investigated. By the determination of the E.M.F. of a lead | lead acetate | lead potassium tartrate | lead cell, the concentration of the lead ions in the tartrate is found to be $10^{-7.4}$, that is, only a trace of the lead can exist in the ion state in this salt. The molecular weight is found by the freezing point method as 301—400; $\text{PbKC}_4\text{H}_3\text{O}_6 = 393$, but as all potassium salts are strongly dissociated it appears that salt exists as double molecules, whilst evidence of hydrolytic dissociation appears from the great increase of conductivity by dilution. A series of similar experiments with Fehling's solution leads to analogous results for the double tartrate of copper and potassium. The constitution of this salt is most probably represented by $[\text{COOK} \cdot \text{CH}(\text{OH}) \cdot \text{CH}(\text{OH}) \cdot \text{COOCu}]_2\text{O}$ with a similar formula for the lead salt. If solutions are prepared by dissolving lead oxide in potassium tartrate in molecular proportion, or by dissolving lead tartrate in potash (1 mol. : 2 mols.), then the whole of the second potash

molecule is not present as such in the solution, and the determination of the concentration of the hydroxyl ions by the use of a manganese dioxide electrode proves this, whilst the copper salt is still poorer in hydroxyl ions. It is hence probable that the potassium of the second potash molecule replaces some of the hydroxylic hydrogen of the tartaric acid radicle.

The optical rotation of solutions of sodium, potassium, and lithium tartrates at varying concentrations, and with varying lead oxide content was next determined, and the results shown by curves. In dilute solutions, the addition of lead oxide in all cases, causes a decrease and finally the inversion of the rotation, but with strong solutions the results are not so simple. An interesting result occurs in some of the lithium solutions where dilution produces an increase of rotation. Salts of the tartar emetic type were next examined, that is double tartrates of potassium with boron, antimony, and arsenic oxides. The experiments are not complete, but show great hydrolytic effect, indicate the absence of antimony ions, and suggest doubled formulæ. The effect of organic hydroxy-compounds in preventing the precipitation of copper and lead by potash was investigated, and the resulting solutions examined in the cases of glycollic, lactic, malic, citric, glyceric, tartaric, and salicylic acids, ethylenic glycol, glycerol, erythritol, mannitol, cane sugar and biuret. In all cases, the concentration of the lead or copper ions is extremely small, and the stability of the compound increases with the alcoholic valency. The constitution is uncertain, but probably in some cases the metal enters the hydroxyl group.

L. M. J.

An Iodine Voltameter for the Measurement of Small Currents. By EDWARD F. HERROUN (*Phil. Mag.*, 1895, [5], 40, 91—94).—The author describes a form of voltameter, especially convenient for the measurement of small currents. The anode consists of a piece of platinum foil, with the leading wire insulated by glass; the electrolyte is a solution of zinc iodide, conveniently prepared by adding potassium iodide to a 15 per cent. solution of zinc chloride, and the cathode consists of a piece of zinc, enclosed in linen or filter paper. The beaker forms a suitable vessel, the anode being at the bottom. The iodine deposited is estimated by sodium thiosulphate (1 c.c. = 0.00657 gram. of iodine = 1 coulomb). The examples given prove the accuracy of the instrument, and the author considers that it possesses the following advantages over ordinary voltameters: (1) freedom from effects of dissolved oxygen, (2) short duration of current necessary, (3) ease and rapidity of estimation and calculation.

L. M. J.

Fundamental Atomic Laws of Thermochemistry. By WILLIAM SUTHERLAND (*Phil. Mag.*, 1895, [5], 40, 1—56).—Thermochemical data in order to be comparable should be the data relating to the formation, at constant volume, of gaseous products from gaseous elements. To obtain such data, the latent heats of vaporisation are required, and the author, therefore, first gives a number of formulæ by means of which these constants may be calculated, and by their means derives the latent heat per gram-atom due to molecular forces, in the case of the metallic elements, and obtains the generalisation

that the latent heat of vaporisation per gram-equivalent, due to molecular force, is approximately a constant or multiple of this constant. The same constants are calculated for a number of halogen compounds by two formulæ, and as the ratio of the results are constant, the relative numbers are probably correct, and the ratio to the actual numbers is obtained by comparison with the directly determined constants in the case of a few chlorides. The heat of formation of inorganic haloid salts is next calculated, and assuming the value $H(RS)$ (that is the heat of formation of the gaseous compound RS from a gaseous metal, R , and a gaseous halogen S) to be of form $(R) + f(RS) + (S)$, where (R) and (S) depend on R and S simply, and $f(RS)$ on both, the result is obtained that $f(RS) = \psi(R) \cdot \psi(S)$, and also $(Cl) = (Br) = (I) = 0$. Hence are derived the values (R) for the metals, the numbers being approximately all simple multiples of 3.8.

Various classes of organic compounds are next determined, a similar treatment being adopted; thus, for example (X being any nucleus), the heat of formation of $X \cdot CH_2 = (X) + (C) + 2(H) + f(XC) + 2f(CH)$, the value $f(XC)$ is found to be independent of (X) , and is hence changed to $f(C \cdot C)$. By the use of Thomsen's data (chiefly) the values for different combinations are then found, the results being—

$$\begin{array}{lll} f(C \cdot C) = 14.0; & f(C \cdot C) = 14.2; & f(C \cdot C) = 0; \\ f(CH) = 15.0; & f(C \cdot O) = 18.5 \text{ and } 15; & f(C \cdot O) = 53; \\ f(C \cdot N) = 0.0; & f(C \cdot N) = 0.0; & f(C \cdot N) = 0; \\ f(OH) = 29.5; & f(O \cdot O) = -10.0; & f(O \cdot N) = 0; \\ f(O \cdot N) = 0.0; & f(NH) = 3.8; & f(SH) = 2.5; \\ f(C \cdot S) = 0.0; & f(C \cdot S) = 9.0; & f(N \cdot N) = 0. \end{array}$$

Most of the numbers are approximately integral multiples of 3.8, so that this evidence favours the hypothesis that atoms in combining chemically give forth integral multiples of a quantity of heat which may be styled the atomic thermochemical unit. L. M. J.

Specific Heat and Boiling Point of Carbon. By JULES VIOLE (*Compt. rend.*, 1895, **120**, 868–869).—The following results have been obtained.

1. Above 1000° the mean specific heat of graphite increases regularly with the temperature, in accordance with the formula

$$C_p = 0.355 + 0.00006t.$$

2. The heat given out by 1 gram of solid graphite in cooling from the temperature of volatilisation to 0° is 2050 Cal.

3. The boiling point of carbon is, therefore, 3600° . H. C.

Specific Heats of Superfused Formic and Acetic acids: Apparatus for the Determination of the Specific Heats of Superfused Liquids. By GUSTAVE MASSOL and GUILLOT (*Compt. rend.*, 1895, **121**, 208–210).—Determinations by means of Regnault's thermocalorimeter gave for the specific heat of liquid formic acid between 20° and 80° , 0.517; of the solid acid between 5° and -5° , 0.656; of the superfused acid between 3° and 26° , 0.514, and between

3° and 7°, 0·544. The specific heat of solid acetic acid between 4° and 8° is 0·618, and of the superfused acid between 12° and 21°, 0·473. In both cases, the specific heat is much higher in the solid than in the liquid state; the specific heat of the liquid diminishes with the temperature; the specific heat of the superfused acid is somewhat higher than that of the liquid, but is of the same order of magnitude. The results are similar to those obtained by Bruner (Abstr., 1895, ii, 378) with thymol and paracresol.

The range of applicability of Regnault's thermocalorimeter may be greatly increased by constructing it after the manner of Walferdin's thermometer, and using mercury, sulphuric acid, or some other liquid boiling at a high temperature instead of alcohol. C. H. B.

Determination of the Critical and Boiling Temperatures of Hydrogen. By KARL OLZEWSKI (*Phil. Mag.*, 1895, [5], 40, 202—210; and *Ann. Phys. Chem.*, 1895, [2], 56, 133—143).—Experiments were performed in order to directly determine the critical temperature of hydrogen by compressing the gas at the temperature of boiling oxygen, and then allowing the pressure to fall to the critical pressure (20 atmos.). In a similar manner, by allowing the pressure to fall to 1 atmos. the boiling point could be determined. A platinum resistance thermometer was employed, the metal wire being very fine (0·025 mm.), in order that it might immediately assume the temperature of the gas. This thermometer was compared with the hydrogen thermometer at 0°, -78·2°, -182·5°, and -208·5°, the results below this being obtained by extrapolation. The critical temperature so obtained is -234·5°, and the boiling point -243·5°. The availability of the method is shown by experiments with oxygen, when the values -118° to -119·2°, and -181·3° to -182·5° were obtained for the critical and boiling temperatures; the determinations obtained otherwise by the hydrogen thermometer being -118·8° and -181·4° to -182·7°. (See also Abstr., 1895, i, 397.) L. M. J.

Some Relations between Temperature, Pressure, and Latent Heat of Vaporisation. By CHARLES E. LINEBARGER (*Amer. J. Sci.*, 1895, [3], 49, 380—396).—The constancy of the quotient of the molecular heat of vaporisation by the absolute temperature at which the vaporisation takes place, or what is commonly known as Trouton's law, has been arrived at in different ways. Still there exist certain discrepancies between the theory and the experimental determination which must be accounted for. Taking all the trustworthy determinations into consideration, it is found that some 70 liquids give an average value for the constant of 20·70, the extreme values being 19·58 and 22·04. But the alcohols, the acids and the nitro-compounds, as well as water and acetone, form exceptions to this rule, the values for the acids and nitro-compounds being too small, and for the alcohols, water and acetone, too large. The cause of this abnormal behaviour is to be found in the association of the molecules of these liquids, as shown by Ramsay, and in the changes which the molecular aggregations undergo during the process of vaporisation.

In the case of the alcohols, water and acetone, the experiments of

Ramsay show that the liquids are made up of molecules in a state of association. On the other hand, the normality of the vapour density and other properties of the vapours of these liquids, show that they consist exclusively of simple molecules. Accordingly, when the liquids are evaporated, there occurs a decomposition of the complex molecules into simpler ones. The heat necessary to convert a molecularly polymerised liquid into its normal vapour consists then of two terms, the heat expended in actually turning the liquid into a gas, and the heat used up in decomposing the molecular aggregations. The molecular heat of vaporisation, and, consequently the constant, becomes greater than the normal, and indeed so much the greater the more complex the liquid molecule.

The case of the acids is different, as here we have reason to suppose that the density of the vapour is abnormal, and that the liquid associated molecule does not undergo much change in passing into the gaseous state. The molecular heat of vaporisation, if calculated from the normal molecular weight, is therefore too low, and the constant only approximates to 20·7, when the mass of the associated molecule is substituted for that of the normal molecule. A similar thing probably holds for the nitro-compounds.

These considerations indicate a method of getting an approximation to the degree of association of a liquid. If any liquid, whose latent heat of volatilisation is known, gives a value for the constant close to 20·7, it is pretty certain that it is normal. If it gives a less value, it is associated in the liquid as well as in the gaseous state; if it gives a greater value, it must be associated in the liquid state alone.

H. C.

The Condensation and the Critical Phenomena of Mixtures of Ethane and Nitrous Oxide. By KUENEN (*Phil. Mag.*, 1895, [5], 40, 173—194).—The results are recorded of experiments on the critical phenomena of various mixtures of the two gases. The ethane was obtained in as pure a state as possible, the foreign admixture being estimated as far below 0·1 per cent.; its critical temperature was 31·95 to 32·05, which is, however, considerably below that of other observers. The critical temperature of the nitrous oxide was 35·95 to 36·05, and the impurity was estimated as below 0·0002. The critical temperatures of the mixtures were found, for the most part, to lie below those of either constituent, thus, 0·1 of ethane lowers the critical temperature to 32°, and a minimum of 25·8° occurs at 0·5 of ethane. The pressures of some of the mixtures are above those of nitrous oxide, a maximum pressure being obtained for 0·2 of ethane, this maximum remaining up to the critical point. In the case of a number of the mixtures, those between 0·2 and 0·5 of ethane, the interesting phenomenon is observed of what the author names "retrograde condensation of the second kind," that is, by compression a vapour phase appears, which begins by increasing, then reaches a maximum, diminishes, and again disappears. The probable occurrence of such a, previously unobserved, phenomenon is discussed and predicted in the first portion of the paper, and its realisation was the chief object of the author's experiments.

L. M. J.

Thermochemistry of Cyanuric acid. By PAUL LEMOULT (*Compt. rend.*, 1895, **121**, 351—354).—Cyanuric acid, contrary to the usual statements, is comparatively insoluble in water, 1000 c.c. at 8° dissolving only 1·5 gram, the solubility increasing slowly with the temperature.

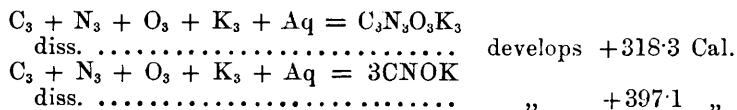
The heat of combustion of the anhydrous acid is 1715·85 Cal., and its heat of formation —165·06 Cal.; heat of dissolution, —3·2 Cal.; heat of hydration, +0·88 Cal.

The heat of formation of the hydrated acid, $C_3N_3O_3H_3 + 2H_2O$, from its elements is +165·9 Cal.; heat of dissolution, —6·88 Cal.

Cyanuric acid is neutral to "methyl-orange," acid to phenolphthaleïn and to litmus, and does not affect the blue CBBB. Phenolphthaleïn becomes violet when the acid is converted into a monosodium salt, and the blue, CBBB, is decolorised when the disodium salt is formed. The heat of neutralisation by sodium hydroxide is +6·78 for the first equivalent, +4·32 for the second, and 1·72 for the third, whilst a fourth equivalent of the alkali develops from 0·15 to 0·5 Cal. With potassium hydroxide, the three equivalents develop, respectively, +6·8, +4·2, and +2·0 Cal. If potassium hydroxide is added to a solution of monosodium cyanurate, the first equivalent develops +4·1 Cal., the second +2·0 Cal., and the third 0·2 Cal.

With ammonia the results are different, and are analogous to those obtained with phosphoric acid; the three successive developments of heat are +6·1, +1·65, and +1·0 Cal. In presence of ammonia, the cyanuric acid retains its power of combining with potassium and sodium hydroxides.

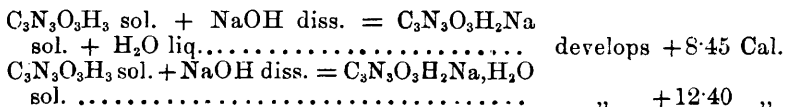
These results indicate that, like phosphoric acid, cyanuric acid is an acid of mixed function,



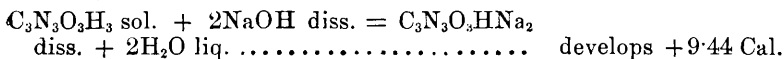
hence the heat of transformation of 3 mols. of dissolved potassium cyanate into 1 mol. of dissolved potassium cyanurate is +27 Cal.

C. H. B.

Thermochemistry of Alkali Cyanurates. By PAUL LEMOULT (*Compt. rend.*, 1895, **121**, 375—378).—Sodium cyanurate, $C_3N_3O_3H_2Na + H_2O$, crystallises in small, white needles, which can only be obtained anhydrous by passing dry air over the finely powdered salt heated at 120—140°. Heat of dissolution of the hydrated salt, —4·91 Cal.; of the hydrated salt, —8·86 Cal.; heat of formation of the hydrate (solid water), +2·55 Cal. The heats of dissolution are independent of the degree of dilution, and consequently the salts are not dissociated by water.



The disodium salt forms silky, anhydrous needles; the heat of dissociation is -1.78 Cal., and is independent of the degree of dilution,



The trisodium salt also crystallises in anhydrous needles; the heat of dissolution is $+1.47$ Cal., and is independent of the degree of dilution; heat of formation from acid and alkali, $+7.93$ Cal.

The monopotassium salt crystallises with $1 \text{ H}_2\text{O}$, which it readily loses at 130° . Heat of dissolution of the anhydrous salt, -8.57 Cal.; of the hydrated salt, -10.85 Cal.; heat of hydration (solid state), $+0.88$. Heat of formation of the solid anhydrous salt from acid and alkali, as above, $+12.17$ Cal., and of the solid, hydrated salt, $+14.45$ Cal.

The dipotassium salt is anhydrous; heat of dissolution, -5.9 Cal. heat of formation from acid and alkali, $+13.7$ Cal.

Attempts to isolate tripotassium cyanurate were not successful, and it would seem that even in solution the formation of this salt is incomplete.

The potassium salts, like the sodium salts, are not decomposed by water. C. H. B.

Heats of Combustion of some β -Ketonic Ethereal Salts. By J. GUINCHANT (*Compt. rend.*, 1895, **121**, 354—357).—The compounds were burnt in the calorimetric bomb.

	Heat of combustion.		
	Constant volume.	Constant pressure.	Heat of formation.
Acetylacetone.....	615.8	616.3	131.2
Methylic cyanacetate.....	472.1	471.9	77.8
Methylic cyanacetoacetate.....	685.5	685.3	122.0
Ethylic cyanacetate.....	629.5	629.7	83.3
Ethylic cyanacetoacetate.....	836.8	837.0	133.6
Methylic malonate.....	552.5	552.5	195.0
Methylic acetylmalonate.....	753.2	753.2	251.9
Ethylic diacetoacetate.....	971.9	972.4	196.0
Methylic acetoacetate.....	593.6	594.0	153.5

In these compounds, the substitution of acetyl for hydrogen raises the heat of combustion by somewhat less than 225 Cal. As in the case of carboxylic acids, the formation of these acid derivatives from their elements is accompanied by an excessive expenditure of energy, a result probably due to the conversion of the acetyl group into the enolic group, $\text{CH}_2\cdot\text{COH}$.

The heats of combustion of these compounds are, as a rule, lower than those of the carboxylic acids of the same composition and molecular weight. C. H. B.

Heat developed by Alcoholic Fermentation. By A. BOUFFARD (*Compt. rend.*, 1895, **121**, 357—360).—Adopting Berthelot's values

for the heats of combustion, and Pasteur's equation for the fermentation of sugar, the total heat developed by the fermentation of each molecule of sugar, $C_6H_{12}O_6$, should be 32.07 Cal. Direct determination gives for 180 grams of sugar, +23.5 Cal., which is considerably below the calculated number; but the difference may be due to errors of experiment. The heat developed lies, however, between 24 and 32 Cal., and it is not necessary to assume so large a development as +71 Cal. in calculating the dimensions of refrigerators. An apparatus using a volume of water equal to half, or to the whole, volume of the wort, ought to suffice in most cases.

C. H. B.

The Dependence of the Volume of Solutions on Pressure.

By GUSTAV TAMMANN (*Zeit. physikal. Chem.*, 1895, 17, 620—636).—Tait's researches on the compressibility of water led to the expression $\Delta v/\Delta p = A/(B + p)$, A and B depending on the temperatures, and for salt solutions he derived the relation $\Delta v/\Delta p = A(B + p + am)$, where m is the quantity of salt dissolved. This expression, however, is only available for dilute solutions, but the volume relations of any solution may be obtained from the internal pressure. If, by solution, the internal pressure increases from κ to $\kappa + \Delta\kappa$, then the volume is that of the solvent at pressure $p = \Delta\kappa$. Hence $\Delta v = \int_0^p dv/dp \cdot dp$ and $v_p = v_0(1 - \int_0^p dv/dp \cdot dp)$. Similarly, the alteration of volume which a solution of internal pressure $\kappa + \Delta\kappa$ experiences, owing to external pressure p , is equal to the volume alteration of solvent due to increase of external pressure from $p_1 (= \Delta\kappa)$ to $p_1 + p$. For aqueous solutions the volume of the solvent is calculable from Tait's expression, $v_p = v_0[1 - A \log(B + p/B)]$. Absolute agreement between calculated and experimental numbers is not to be expected, as the assumption is made that $\Delta\kappa$ is not altered by the pressure, and that no chemical change occurs. The values of v_p for water are first compared with the experimental determinations of Amagat; the agreement is close, the calculated values being probably the more accurate. The calculated and observed values (Tait's) are then compared in the cases of solutions of sodium chloride, magnesium sulphate, ammonium sulphate, potassium iodide, and barium chloride for pressures up to 457 atmos., and the results agree within 3 per cent. of the total volume alteration. The expression is also tested by means of Röntgen's and Schneider's determinations, and its validity again established (*Abstr.*, 1895, ii, 307).

L. M. J.

Solubility of Mixed Crystals. WILLEM STORTENBEKER (*Zeit. physikal. Chem.*, 1895, 17, 643—650).—The various cases of solubility curves of mixed hydrated crystals are illustrated, the molecular percentages of the two constituents serving as ordinates and abscissæ. The curve may be continuous or it may exhibit breaks, owing to mixtures existing in a labile state. Three classes of curves are illustrated. (1) The solubility isothermals do not cut as in the case of

$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$, $\text{ZnSO}_4 \cdot 6\text{H}_2\text{O}$; here the isothermal of the latter series is throughout labile, and lies outside that of the more hydrated crystals. (2) The isothermals cut as in the case of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, $\text{FeSO}_4 \cdot 5\text{H}_2\text{O}$ and $\text{CuSO}_4 \cdot 7\text{H}_2\text{O}$, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$. As when the curves cut, that nearer the origin is the more stable, there are two partial curves for the stable form. Similarly, if the isothermal itself has a break, the curve may consist of three broken portions. The curves for three classes of mixed crystals are also illustrated, but in this case the variety of forms is very great.

L. M. J.

Estimation of the velocity of Chemical Attraction. By NICOLAE TECLU (*J. pr. Chem.*, 1895, [2], 52, 277—284).—The flame of a mixture of inflammable gases, such as hydrogen and oxygen, remains stationary when the velocity of the mixed gases is equal to the rate at which the gases combine; and if the mixture consists of equivalent masses of the combining gases, this rate of combination must bear some ratio to the time which elapses while the atoms are coming within the sphere of their mutual attraction. Measurements of this rate of movement cannot be made with any degree of accuracy when the combustion is occurring in a tube, because a variety of conditions, for instance, the enhanced temperature and the presence of the product of the combustion, affect the results. The author has sought to measure the rate of issue of hydrogen from a jet into air and of air from the same jet into hydrogen at the moment when the gas ignites at the jet, the ignition being effected by a small gas flame held immediately below the issuing stream of gas at a point 1 cm. from the jet. This rate of issue should be a measure of the velocity of attraction of hydrogen for oxygen on the one hand and of oxygen for hydrogen on the other hand.

The hydrogen, or air, was confined in a vessel over water at a pressure of about 300 mm. of mercury. A stopcock controlled the rate of issue of the gas from the jet, and a manometer enabled the pressure in the vessel to be recorded at the desired moment. The diameter of the jet was 0.291 mm. To create an atmosphere of hydrogen around the jet when the vessel contained air, a hydrogen delivery tube, terminating in a slit 2 mm. wide and 6 mm. long, was held with the length of the slit parallel to and immediately below the stream of issuing gas, so that the latter passed through the slow stream of hydrogen on its way to the ignition flame.

The rate of issue of the gas is calculated from the formula

$$v = \sqrt{2g \frac{h - h_1}{s}},$$

where v = velocity of the gas in metres per second,
 g = gravity constant (9.8085 at Vienna),
 h = pressure of issuing gas in metres of air,
 h_1 = pressure of gas into which the issue occurs, in metres of air.
 s = specific gravity of issuing gas.

As a mean of ten observations of pressure, in as many experiments,

the value $v = 813.71$ was obtained for hydrogen issuing into air. Taking the volume of the air as 4.8204 times that of the oxygen contained in it, and multiplying by the contraction-coefficient (0.8), v becomes 3137.93 metres per second, and represents the velocity of attraction (*Attractions-Geschwindigkeit*) of hydrogen for oxygen.

In another series of observations in which air issued into hydrogen, the velocity of attraction of oxygen for hydrogen, similarly calculated, was found to be 774 metres per second.

Embodying the above velocities in the kinetic energy equation $E = mv^2/2$, the values 4923522 metre-kilos. and 4792608 metre-kilos. are obtained for the chemical atom-energy of hydrogen and oxygen respectively; these values may be regarded as representing a constant. By substituting the former value for E in the equation, the value of v for any other gas may be ascertained. The chemical atom-energy constant being known, the energy value of any combination may be calculated; thus the combination of hydrogen and chlorine consisting in a union of two atoms, its energy value per kilo. of hydrogen should be 2×4923522 metre-kilos, or $9847044 \div 424 = 23224$ Cal. The determined value is 23783 Cal.

A. G. B.

Equilibrium in the System $\text{HgO}—\text{SO}_3—\text{H}_2\text{O}$. By C. HOITSEMA (*Zeit. physikal. Chem.*, 1895, 17, 651—677).—The three components of this system may form the solid compounds HgSO_4 ; $\text{HgO}, \text{SO}_3, \text{H}_2\text{O}$; $3\text{HgO}, 2\text{SO}_3, 2\text{H}_2\text{O}$; and $3\text{HgO}, \text{SO}_3$, the latter being well known as turpeth mineral. The compound $4\text{HgO}, \text{SO}_3$, stated to occur, could not be prepared by the authors. The determination of the equilibrium relations were performed by adding the solid compounds to acids of various concentrations in a flask maintained at a constant temperature (25° or 50°), and kept in rotation for three hours, after which portions of the solution were withdrawn and analysed. The first branch of the 25° curve is that with $3\text{HgO}, \text{SO}_3$ as solid phase, and here the HgO and SO_3 molecular percentage increases from 1.2 and 0.33 to 4.3 and 2 respectively; at this point, the curve cuts the second branch, for which the solid phase is $3\text{HgO}, 2\text{SO}_3, 2\text{H}_2\text{O}$. Here the molecular percentage of HgO varies but slightly with increasing acid content, so that the curve drawn with the percentages of HgO as ordinates is almost horizontal. In three cases, a labile equilibrium was obtained, the $3\text{HgO}, \text{SO}_3$ solid phase persisting. The second curve cuts that of the solid phase $\text{HgO}, \text{SO}_3, \text{H}_2\text{O}$ at 6.77 per cent. SO_3 and 2.02 per cent. HgO , which phase persists to 8.1 per cent. SO_3 , 0.6 per cent. HgO . The quantity of the oxide dissolved becomes for this curve very small with increasing acid content. The results also, where comparable, agree very satisfactorily with those of Le Chatelier. In the observations at 50° , the third branch disappears and the other branches show a region in which phases 1, 2; 2, 4; and 4, 1 may coexist, while the curves further indicate that solutions of turpeth mineral and of HgSO_4 as solid phase will precipitate the solid by warming, but this does not hold for cases in which the solid phase is $3\text{HgO}, 2\text{SO}_3, 2\text{H}_2\text{O}$ where increase of temperature causes a transition to either $3\text{HgO}, \text{SO}_3$ or to HgSO_4 . A similar transition from $\text{HgSO}_4, \text{H}_2\text{O}$ to HgSO_4 also evidently occurs. Since a line equi-

distant from the two axes does not cut branch 4, it is evident that the compound HgSO_4 is not soluble in water without decomposition. The paper concludes with a short discussion of possible causes of this decomposition and of the hydrolytic formation of the basic salt, $3\text{HgO}, \text{SO}_3$.

L. M. J.

The Colour of the Ions as a Function of the Atomic Weight.

By JULIUS THOMSEN (*Zeit. anorg. Chem.*, 1895, **10**, 155).—With regard to the arrangement of the elements in a periodic system, described by Carey Lea (*Abstr.*, 1895, ii, 441) on the basis of the colour of the ions, the author points out that the form of the periodic system published by him (*Zeit. anorg. Chem.*, 1892, **9**, 192) is in accordance with a very simple relation between the colour of the ions and the atomic weights. Those ions only are coloured which belong to the middle members of the large series. The two first series, with 7 members, contain no coloured ions; the two next, with 17 members, contain in each series 7 to 8 coloured ions (titanium to copper and niobium to silver), and in the 5th series, with 31 members, the group with coloured ions (cerium to gold) is in the middle of the series.

E. C. R.

Supposed Group of Inactive Elements. By JULIUS THOMSEN (*Zeit. anorg. Chem.*, 1895, **9**, 283—288).—If the chemical character of the elements is a periodic function of the atomic weights, such a function must follow the ordinary general laws. In periodic functions, the change from negative to positive values or the reverse can only take place by a passage through zero or through infinity; in the first case the change being a gradual and in the second case a sudden one. The first case corresponds with the gradual change in electrical character with rising atomic weight in the separate series of the periodic system, and the second case corresponds with the passage from one series to the next. It therefore appears that the passage from one series to the next in the periodic system should take place through an element whose electrical character is $\pm \infty$, and which is therefore electrically indifferent. The valency of such an element would be zero, and therefore in this respect also it would represent a transitional stage in the passage from the univalent electronegative elements of the seventh to the univalent electropositive elements of the first group. This indicates the possible existence of a group of inactive elements with the atomic weights 4, 20, 36, 84, 132, and 212.

H. C.

Argon, Prout's Hypothesis and the Periodic Law. By EDWIN A. HILL (*Amer. J. Sci.*, 1895, [3], **49**, 405—417).—If argon be an element, its properties indicate that its place in the periodic classification is between fluorine and sodium, with an atomic weight of 20. Yet the specific heat ratio of 1.66 points to an atomic weight of 40, if such a ratio necessarily involves monatomicity. The weak point in the assumption that it does, lies in the view taken that the molecular encounter involves actual contacts, which is not a necessary assumption in the kinetic theory of gases. The greater the force of aggregation, and the smaller the distance between the atoms com-

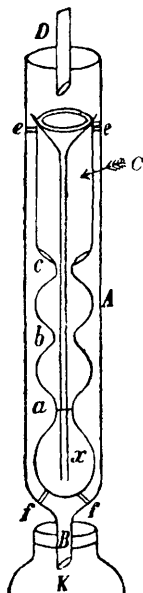
pared to the imaginary molecular diameter or least distance of approach, the less the tendency for internal rotation.

The author points out that in the determinations of the combining ratio of hydrogen and oxygen, there is great probability of the hydrogen used, or of the water formed having been contaminated with argon. The effect of this would be to decrease the value for oxygen, so that the atomic weight would approximate to 16, the whole number required by Prout's hypothesis.

H. C.

A New Extraction Apparatus. By J. J. L. VAN RIJN (*Ber.*, 1895, **28**, 2387).—The apparatus, consisting of a wide glass tube, *A*, and an extraction vessel, *C*, supported at *e* and *f*, is intended for the extraction of liquids, and is so arranged that the extraction is carried out at a temperature close to that of the boiling point of the extracting liquid. The vapour condenses in *D*, drops into the funnel tube, and bubbling up through the liquid in the bulb *x*, ultimately runs out through the holes at *c*, back into the extraction vessel *K*.

A. H.



Inorganic Chemistry.

Conversion of Chlorine into Hydrogen Chloride. By RICHARD LORENZ (*Zeit. anorg. Chem.*, 1895, **10**, 74—77).—Chlorine is completely converted into hydrogen chloride by passing it, mixed with steam, through a tube filled with coke, and heated to a faint red heat. The action is expressed by the equation $2\text{Cl} + \text{H}_2\text{O} + \text{C} = 2\text{HCl} + \text{CO}$, and so complete is it that the gases issuing from the hot tube do not contain sufficient chlorine to give a reaction with potassium iodide and starch. After absorption of the hydrogen chloride by means of water, the residual gas is almost pure carbonic oxide, containing only a very small quantity of carbonic anhydride.

E. C. R.

Crystallisation of Bromine. By HENRYK ARCTOWSKI (*Zeit. anorg. Chem.*, 1895, **10**, 25—26).—Bromine crystallises from a very concentrated solution in carbon bisulphide at -90° in slender, carmine red needles, having a somewhat similar appearance to chromic anhydride. The crystals are pure bromine. Bromine, when sufficiently cooled, solidifies to a dark brown mass, which has a crystalline fracture, but not so well defined a metallic lustre as iodine.

E. C. R.

Compound of Selenium with Arsenic. By A. CLEVER and WILHELM MUTHMANN (*Zeit. anorg. Chem.*, 1895, **10**, 117—147).—The authors attempted to prepare compounds of arsenic acid in which the oxygen is partially replaced by selenium. For this purpose, arsenious acid dissolved in concentrated potassium hydroxide was mixed with selenium, also dissolved in potassium hydroxide. A complicated reaction takes place, a small quantity of selenium is deposited, but the only compound which the authors were able to isolate was a potassium polyselenide, described below.

Potassium oxyselenoarsenate, $K_6As_2Se_3O_3 + 10H_2O$, is obtained by treating arsenic pentaselenide with potassium hydroxide. The arsenic pentaselenide (5 grams), prepared by melting a finely ground mixture of arsenic and selenium in a porcelain crucible, is gradually added to a concentrated solution of potassium hydroxide (10 grams), the mixture being cooled with ice; it is then filtered into absolute alcohol (300 c.c.), and the orange-red, crystalline mass thus obtained is washed with alcohol and dried on a porous plate. It is analogous to the salt $Na_6As_2S_3O_5 + 24H_2O$, described by Geuther. It rapidly decomposes and darkens on exposure to air and moisture, selenium being deposited; it dissolves easily in water, forming a greenish-yellow solution, and then decomposes rapidly with deposition of red selenium. With salts of the heavy metals it gives dark, amorphous precipitates; with barium salts, a reddish-white compound, which decomposes very rapidly. When treated with acids, it yields arsenic pentaselenide.

Arsenic pentaselenide, As_2Se_5 , prepared by melting its constituents together, has properties similar to those of Ülsmann's triselenide. When heated in the air, it decomposes, and red selenium and a greyish-black sublimate are formed. If prepared by decomposing the preceding compound with acid, it forms a reddish-brown powder. It dissolves to a greenish-red solution in alkalis and ammonia, and is reprecipitated unchanged by acids; it is insoluble in dilute acids and concentrated hydrochloric acid, and is slowly decomposed by warm, dilute nitric acid, very rapidly by cold, fuming nitric acid, whereby arsenic and selenious acid are formed. It is insoluble in water, alcohol, ether, and carbon bisulphide, and has neither taste nor odour.

Potassium metaselenoarsenate, $KAsSe_3 + 2H_2O$, is obtained by adding arsenic pentaselenide to a solution of selenium in potassium hydroxide; the mixture, after being heated for some time, is filtered into alcohol, a small quantity of water is added, in order to dissolve other compounds which are formed at the same time, and the product is then dried on a porous plate. It crystallises in reddish-yellow prisms, and is easily soluble in hot water, but the solution soon decomposes, with deposition of selenium; alkaline solutions are somewhat more stable. Acids precipitate arsenic pentaselenide from the aqueous solution with evolution of hydrogen selenide. With lead and silver salts, it gives a black precipitate; with barium salts, a reddish-white precipitate, which rapidly decomposes.

Potassium thioselenoarsenate, $K_6As_2Se_5S_3 + 12H_2O$, is prepared by adding arsenic pentasulphide to a solution of potassium sulphide,

heating the mixture to boiling, and filtering the solution into alcohol; the compound then crystallises out in orange-red needles. It is unstable on exposure to air and moisture, melts to a reddish-yellow liquid at the warmth of the hand, and is fairly stable in aqueous solution; the aqueous solution, when treated with acids, gives a brownish-red precipitate of the pentaselenide mixed with sulphur, hydrogen sulphide being evolved.

Sodium oxyselenoarsenate, $3\text{Na}_2\text{Se}, 3\text{Na}_2\text{O}, \text{As}_2\text{O}_3 + 50\text{H}_2\text{O}$, is obtained by warming arsenic pentaselenide with a concentrated solution of sodium hydroxide; a new hydrate of sodium monoselenide, described below, is at first precipitated, but on filtering, and mixing the filtrate with alcohol, the oxy-compound crystallises out in white, elongated prisms, which are fairly stable on exposure to air. It is easily soluble in water; acid precipitates selenium from the solution and an arsenic selenide is not formed. With lead and silver salts, it gives a black precipitate; and with barium chloride, a white, amorphous precipitate which is easily soluble in warm water.

Sodium selenoarsenite, $\text{Na}_3\text{AsSe}_3 + 9\text{H}_2\text{O}$, is formed together with other salts when arsenic pentaselenide is boiled with a solution of selenium in sodium hydroxide; on concentrating the filtered solution in a vacuum, a mixture of white needles and orange-red tetrahedra is obtained. On separating these by levigation, a small quantity of the tetrahedra are obtained. It is unstable on exposure to air, becoming coated with grey selenium; it is easily soluble in water, and the brown solution when treated with dilute acids gives a brownish-red precipitate with evolution of hydrogen selenide.

Sodium thioselenoarsenate, $\text{Na}_6\text{As}_2\text{Se}_3\text{S}_3 + 18\text{H}_2\text{O}$, prepared in a similar way to the corresponding potassium salt, crystallises in golden-yellow spangles, or in beautiful, long needles which are fairly stable, but slowly darken and decompose on exposure to air. It is easily soluble in water; and acids precipitate a brown compound from the dark-brown solution with evolution of hydrogen sulphide; towards acids and salts of the heavy metals, it behaves like the potassium salt.

Potassium triselenide, $\text{K}_2\text{Se}_3 + 2\text{H}_2\text{O}$, is obtained, as previously stated, in brown needles, when potassium selenide is mixed with arsenious acid dissolved in alkali; the crystals rapidly decompose and become coated with grey selenium on exposure to air. It dissolves in water, and the solution when treated with acids, yields selenium and hydrogen selenide.

Sodium monoselenide, $\text{Na}_2\text{Se} + 10\text{H}_2\text{O}$, obtained as mentioned above, crystallises in beautiful white needles which rapidly turn red, then brown, and become coated with grey selenium; it is easily soluble in water, but insoluble in alkali hydroxides. It evolves hydrogen selenide on exposure to the air, or when treated with dilute acids; melts to a brown liquid when warmed, and has the properties assigned to the sodium selenide obtained by Fabre. E. C. R.

Helium and Argon. By HEINRICH KAYSER (*Chem. News*, 1895, 72, 89).—The author records the discovery of helium in the free state in nature. In the springs of Wildbad, in the Black Forest, bubbles of gas rise up, which, according to an old analysis of Fehling, contain

96 per cent. of nitrogen. An analysis of this gas showed that after sparking with excess of oxygen and removal of the residual oxygen with pyrogallol, a residue was obtained which gave the spectra of argon and helium, the latter being evidently present in quantity. Runge and Paschen found two substances in the gas from clèveite and bröggerite, and both these elements appear to be represented in the Wildbad gas. As a place has here been found in which the two gases represented by the name helium are liberated and stream into the atmosphere, it follows that these must be normally present in the atmosphere. The author has found this to be the case, and that argon prepared from the air of Bonn contains helium, the presence of the D_3 line in the spectrum being most marked. H. C.

A Possible Compound of Argon. By WILLIAM RAMSAY (*Chem. News*, 1895, 72, 51).—By making an arc between two thin carbon rods, in an atmosphere of argon for some four hours, the volume of the gas increased about one-fifth, and was not altered by exposure to water, to caustic soda, or to ammoniacal cuprous chloride. It gave, in addition to a faint argon spectrum, a luminous, finely channelled spectrum, with certain lines not coincident with argon lines (see Crookes, this vol., ii, 2). D. A. L.

Fluorides and Oxyfluorides of Potassium. By G. MARCHETTI (*Zeit. anorg. Chem.*, 1895, 10, 66—73).—Anhydrous potassium titanofluoride, K_2TiF_6 , is prepared by adding the theoretical quantity of potassium hydrogen fluoride to a solution of titanium dioxide in an excess of hydrogen fluoride. It crystallises in small, very lustrous leaflets, which are denser than the crystals of the hydrated fluoride, $K_2TiF_6 \cdot H_2O$. It can be crystallised without change from hot hydrofluoric acid, but when dissolved in water it is completely converted into the hydrated salt. Conversely, when the hydrated salt is dissolved in concentrated hydrofluoric or hydrochloric acid, it is converted into the anhydrous salt.

The normal potassium fluoride compounds of niobium, molybdenum, and tungsten, of the formulæ $NbO_2F_2 \cdot 2KF \cdot H_2O$, $MoO_2F_2 \cdot 2KF \cdot H_2O$, and $WO_2F_2 \cdot 2KF \cdot H_2O$, respectively, behave in the same way.

The oxyfluoride of molybdenum, $MoO_2F_2 \cdot 2KF \cdot H_2O$, obtained by adding the theoretical quantity of potassium hydroxide to a solution of molybdic anhydride in hydrofluoric acid, taking care that the mixture remains acid, crystallises from hot hydrofluoric acid in short, lustrous prisms of the composition $MoO_2F_2 \cdot 2KF$. The salt described by Delafontaine (*Arch. Sci. Phys.*, 1867, 30, 244), $MoO_2F_2 \cdot KF \cdot H_2O$, is probably a mixture of the two preceding salts, and, according to the author's results may also contain the oxyfluoride $MoOF_4 \cdot KF$.

The double fluoride of tungsten, $WO_2F_2 \cdot 2KF \cdot H_2O$, is obtained in a similar way to the molybdenum salt. The anhydrous salt crystallises in groups of large tablets. E. C. R.

Some Alkali Phosphides. By C. HUGOT (*Compt. rend.*, 1895, 121, 206—208).—When liquefied ammonia is brought in contact

with a mixture of known quantities of red phosphorus and sodium or potassium, the sodammonium or potassammonium which is first formed is decomposed by the phosphorus with liberation of hydrogen, and the product remains in solution in the excess of ammonia. Potassium yields a red compound, $P_3K, 3NH_3$, which when heated at 180° loses all its ammonia, and leaves a brownish-red mass of the phosphide, P_3K . Sodium yields a red product, $P_3Na, 3NH_3$, which at 180° loses all its ammonia, and leaves the phosphide P_3Na . The potassium compound is not obtained quite pure, since potassamide is slightly soluble in liquefied ammonia, but this difficulty is not experienced in the case of the sodium compound. Both phosphides are decomposed by moist air, with liberation of hydrogen phosphide. Their other properties will be described subsequently.

C. H. B.

Determination of the Atomic Weight of Zinc. By THEODORE W. RICHARDS and ELLIOT F. ROGERS (*Zeit. anorg. Chem.*, 1895, **10**, 1—24).—The authors have determined the atomic weight of zinc from the ratio of silver to zinc bromide and silver bromide to zinc bromide.

The specific gravity of zinc bromide was found to be 4.219 at 20° . The zinc bromide employed in the first series of determinations was prepared by dissolving pure zinc oxide in pure hydrogen bromide, the pure zinc oxide being prepared by dissolving commercially pure zinc in dilute sulphuric acid, and allowing the solution to remain some weeks in contact with an excess of the metal. The filtered solution is then slightly acidified with sulphuric acid and treated with pure hydrogen sulphide until a considerable quantity of pure white precipitate is formed, and the filtrate from this is treated with chlorine water and fractionally precipitated with pure soda. The first precipitate, which contains iron and manganese is discarded, but the second precipitate after being well washed with water, is dissolved in pure nitric acid, treated with an excess of zinc carbonate, and filtered; the filtrate is treated with a small quantity of ammonium carbonate, and, after filtration, the zinc is precipitated with ammonium carbonate. The basic zinc carbonate thus obtained is washed, heated in a platinum crucible by means of a spirit flame, and again washed and dried. The hydrogen bromide was prepared according to well-known methods, and purified by fractional distillation.

In the determination of the atomic weight, great care must be taken that the zinc bromide is free from every trace of water; the method employed is that already described by the author for the analysis of strontium bromide (*Abstr.*, 1895, ii, 314). The pure recrystallised or sublimed zinc bromide is heated for some time in a platinum boat in a current of nitrogen containing hydrogen bromide, by which means all the water is removed without the slightest formation of oxybromide; the dry salt is then quickly transferred to a desiccator and weighed. It is dissolved in water, precipitated with a slight excess of silver dissolved in nitric acid, and the silver bromide thus obtained is collected in a Gooch's crucible, and weighed. In a second series of determinations, the filtrate was concentrated,

and the excess of silver determined by precipitation with hydrobromic acid. The first series of five experiments gave $Zn = 65.459$. The second series of four experiments gave $Zn = 65.430$ from the ratio $Ag_2 : ZnBr_2$, and $Zn = 65.425$ from the ratio $2AgBr : ZnBr_2$. The silver bromide obtained in the last four experiments gave 57.444 per cent. Ag, which shows that the hydrogen bromide employed was free from chlorine and iodine, and that the precipitate contained no included zinc bromide.

In the third series of experiments, the zinc bromide was prepared by dissolving pure electrolytic zinc in pure bromine. A solution of zinc sulphate is prepared as described above, but after the treatment with chlorine, pure soda is added, until a small precipitate is formed, and the mixture is allowed to remain for some days, shaking occasionally; the precipitate is then filtered off, and the zinc sulphate crystallised from hot water. The solution of this zinc sulphate after being allowed to remain two days in contact with pure electrolytic zinc in a platinum dish, is filtered, treated with ammonia, and electrolysed with a current of 1 to $1\frac{1}{2}$ ampères; the zinc crystals formed being washed with ammonia, then with hydrochloric acid, and finally with water. The zinc is then dissolved in bromine, the solution filtered through asbestos, and the excess of bromine eliminated by heating on the water bath; finally the zinc bromide is either sublimed or distilled in a special apparatus which is figured in the original paper, and so arranged that the sample to be analysed is collected in platinum vessels. The zinc bromide is first dried at a gentle heat in an atmosphere of carbonic anhydride, then at a temperature slightly above its melting point in carbonic anhydride mixed with hydrogen bromide, and finally at 150° in a current of air until the exit gases show no trace of carbonic anhydride or hydrogen bromide. It is then weighed, dissolved in water, and precipitated in the dark with silver dissolved in nitric acid; two equivalent solutions of silver and hydrogen bromide are employed to determine the point at which an opalescence of equal intensity is produced in the clear supernatant liquid. Finally a slight excess of silver nitrate is added, and the precipitate collected in a Gooch's crucible and weighed. The mean of three experiments gave $Zn = 65.402$ from the ratio $ZnBr_2 : 2Ag$, and the mean of three other experiments gave $Zn = 65.406$ from the ratio $ZnBr_2 : 2AgBr$.

The author concludes that when $O = 16$ the most probable value for the atomic weight of zinc is 65.40.

E. C. R.

Electrolytic Preparation of Zinc and Lead. By RICHARD LORENZ (*Zeit. anorg. Chem.*, 1895, **10**, 78—116).—*Electrolysis of Fused Zinc Chloride.*—The chief difficulty to be overcome in the electrolysis of zinc chloride, is to obtain the salt entirely free from water. The zinc chloride, which still contains water, is placed in a V-tube of combustion glass, and heated to quiet fusion. A carbon electrode is placed in each arm of the tube. Directly the current is started, a brisk evolution of gas, due to the presence of water, takes place at both electrodes; the gas evolved at the positive electrode is at the commencement hydrogen chloride, but after some time chlorine is evolved;

meanwhile the evolution of gas at the negative electrode diminishes, and zinc begins to be deposited. During the deposition of the first few drops of metal, a brisk evolution of hydrogen takes place at the negative electrode. As the zinc which is deposited at first is not pure, but contains lead and other metals which may be present, the molten electrolyte is poured off into a similar V-tube as soon as the less positive metals have been deposited, and the electrolysis is continued; pure zinc is then deposited. The electrolyte, which now consists of pure zinc chloride, is a clear, limpid, highly refractive liquid, under which the molten zinc appears like mercury. It solidifies, on cooling, to a white, porcelain-like mass, and is the most hygroscopic substance the author has worked with.

Fused lead chloride is easily electrolysed in a similar way.

Fused cadmium chloride is not so easily electrolysed; chlorine is at once evolved at the anode, and at the cathode brownish-black clouds which dissolve in the electrolyte, whilst a small quantity of cadmium is deposited. The electrolyte contains a lower chloride of cadmium, which can be obtained as a crystalline metallic powder by lixiviating the electrolyte with water; this compound is difficult to dissolve in hydrochloric acid, and the solution does not at first give a precipitate with hydrogen sulphide, but, after some time, a yellow precipitate is suddenly deposited.

In the electrolysis of fused silver chloride, the silver is deposited as a brown mass, and when a small quantity of melted zinc or lead is placed in contact with the cathode, the silver dissolves in the molten metal. Silver chloride dissolves in zinc and lead chlorides, and, on subjecting the mixture to electrolysis, the silver is deposited first. The silver is also deposited when a zinc rod is placed in molten zinc chloride containing silver chloride.

Copper chloride, dissolved in zinc chloride, in which, however, it is only slightly soluble, can be electrolysed by employing a cathode of molten zinc, when all the copper is obtained as a zinc copper alloy.

Mixtures of zinc, silver, lead, copper, and cadmium chlorides on fusion give colourless electrolytes, which are easily manipulated. The addition of lead chloride to zinc chloride greatly increases the ease with which the fused salt is dehydrated by heat alone, and magnesium and calcium chloride produce the same effect. When such mixtures of fused metallic chlorides are electrolysed, the metals are deposited one after the other, and can be obtained pure by fractional electrolysis.

With a mixture of lead and zinc chlorides containing cadmium chloride, after 20 ampère-minutes, the metallic regulus contained 97.34 per cent. lead, 1.35 per cent. cadmium, and 1.30 per cent. zinc; after 175 ampère-minutes, it contained 1.30 per cent. lead, 2.55 per cent. cadmium, and 96.15 per cent. zinc, and after 335 ampère-minutes, pure zinc was deposited. With a mixture of lead, silver, and zinc chlorides, a separation of the silver and lead cannot be obtained; after 2.5 ampère-minutes, the regulus contained 60.6 per cent. silver, 8 per cent. lead, and 7.5 per cent. zinc; after 7.5 ampère-minutes, 80 per cent., 5 per cent., and 14 per cent. respectively, and

after 27.5 ampère-minutes, 0.49 per cent., 96.96 per cent., and 2.5 per cent.; after 172.5 ampère-minutes, pure zinc was obtained. With a mixture of zinc and silver chlorides, and employing a cathode of molten lead, the silver was easily separated; with a cathode of molten zinc, however, after 330 ampère-minutes, the electrolyte still contained traces of silver. With a mixture of copper and zinc chlorides, and employing a cathode of molten zinc, copper is deposited at once, before the current is started, and after 90 ampère-minutes pure zinc is obtained.

A large number of experiments, fully described in the original paper, show that 0.9 volt is sufficient to deposit zinc by this method, and a slightly lower voltage to deposit lead. The deposition of zinc is theoretical, 435.89 ampère-minutes deposited 9 grams, whereas, theoretically, 8.86 grams should have been deposited.

The author bases a method of winning zinc and lead from their ores on the results of the above experiments. Ores containing chiefly zinc, with lead and small quantities of silver and cadmium, are roasted and treated with hydrochloric acid. When excess of acid is employed, the iron and aluminium are precipitated from the solution by the addition of zinc oxide, and the purified liquor evaporated and the residue fused. Ores which contain chiefly lead are treated with dilute acetic acid, and the lead and silver precipitated from the solution by the addition of sufficient hydrochloric acid. After separation of the lead and silver chlorides, the liquor is again used to lixiviate fresh portions of ore until it becomes saturated with zinc acetate. The acetic acid is then removed by treating the liquor with hydrogen chloride and distilling, and again used with fresh portions of the ore. A description of an apparatus suitable for carrying out the operation on a technical scale is given. The chlorine evolved during the electrolysis is converted into hydrochloric acid by the method described by the author (this vol., ii, 17).

E. C. R.

Chromates and Dichromates of the Heavy Metals. By JUL. SCHULZE (*Zeit. anorg. Chem.*, 1895, **10**, 148—154).—In contradiction of the results obtained by Krüss and Unger (*Abstr.*, 1895, ii, 355), the author has obtained the following chromates and dichromates in a crystalline form.

Copper dichromate, $\text{CuCr}_2\text{O}_7 + 2\text{H}_2\text{O}$, is obtained by saturating a cold solution of chromic acid, previously freed from sulphuric acid, with copper carbonate, and evaporating the greenish-brown solution under the air pump. It separates in very lustrous, black crystals, is slightly hygroscopic, and dissolves easily, and without decomposition, in cold water; when heated with water, however, it decomposes, and is partially converted into a brown compound. It is identical with the salt described by Dröge (*Annalen*, **101**, 39).

Copper chromate is obtained by heating the dichromate with copper oxide in a sealed tube at 220° . It crystallises in minute, brownish, transparent prisms, insoluble in water, but easily soluble in acids or in chromic acid; when boiled with water, it gradually decomposes, and yields the dichromate and the salt $3\text{CuO}, \text{CrO}_3 + 2\text{H}_2\text{O}$.

Cadmium dichromate, $\text{CdCr}_2\text{O}_7 + \text{H}_2\text{O}$, obtained in the same way

as the copper salt, separates in orange-brown, cubic crystals, and dissolves easily, and without decomposition, in water.

Cadmium chromate, obtained by heating the dichromate with cadmium hydroxide, in a sealed tube, at 200° , separates as a bright, orange-yellow powder, which appears crystalline under the microscope. When boiled with water, it yields the dichromate and a brownish-yellow powder. The filtrate obtained in the preparation of the chromate, when allowed to remain for some time, deposited crystals containing $2\text{H}_2\text{O}$, and this is the only chromate of the heavy metals which contains water of crystallisation.

Zinc dichromate, $\text{ZnCr}_2\text{O}_7 + 3\text{H}_2\text{O}$, crystallises in dark, reddish-brown, crystalline crusts, and has similar properties to the above salts. *Zinc chromate* is obtained as a fine powder, which appears crystalline under the microscope; it is insoluble in water, easily soluble in acids, and is decomposed by boiling with water, yielding the dichromate and a greyish-yellow, crystalline basic chromate.

Manganese carbonate dissolves in a cold solution of chromic acid in the proportion of 1 to 2, but the product obtained on evaporation was not crystalline. It formed a black powder containing chromic oxide. Cobalt and nickel oxides also dissolve easily in a cold solution of chromic acid in the ratio of 1 to 2.

The author has attempted to prepare a chromic acid alum by adding potassium chromate to a solution of alumina in chromic acid, but in all cases potassium dichromate was formed. E. C. R.

Carbides of the Metals of the Rare Earths. By OTTO PETERS-SON (*Ber.*, 1895, **28**, 2419—2422).—When the oxides of yttrium and lanthanum are mixed with powdered carbon and reduced in a carbon crucible in the electric arc, carbides of the formula MC_2 are produced. The end of the reduction is rendered evident by the appearance of flames, arising from the vapour of the metal, which show a very brilliant spectrum, in which the most conspicuous lines are reversed. The carbides are crystalline and brittle, and have a golden yellow colour when freshly broken, but the surface is almost as rapidly attacked by the moisture of the air as a fresh surface of metallic sodium, a thin grey layer of oxide being formed. They are decomposed by water with evolution of hydrogen and carburetted hydrogen, the hydroxide of the metal and graphitic carbon being deposited. *Yttrium carbide* has the sp. gr. 4.185, whilst that of *lanthanum carbide* is 4.718; both of these carbides contain 2—3 per cent. of graphitic carbon, which has not been included in the composition on which the formula is based. Drawings are given of the simple electric furnace employed. A. H.

Crystallised Anhydrous Manganese Sulphide. By A. MOURLOT (*Compt. rend.*, 1895, **121**, 202—203).—When well dried, amorphous manganese sulphide, mixed with a small quantity of sulphur, is subjected to the action of an arc from a current of 40 amperes and 20 volts for about 20 minutes, the upper part of the fused mass, after cooling, is distinctly crystalline. With more powerful currents, the sulphide does not crystallise so well. The

action of carbon bisulphide and hydrogen sulphide at a high temperature on manganese prepared in the electrical furnace yields the amorphous sulphide only.

The crystallised sulphide is in the form of small, transparent, deep green octahedra, which have no action on polarised light; sp. gr. = 3.92, hardness = 3.5 to 4. The fused sulphide is sufficiently hard to scratch quartz; sp. gr. = 4.06. The crystallised sulphide, prepared in the manner indicated, is identical in composition and physical properties with *alabandine*; it has practically the same chemical properties as the amorphous sulphide, but is less readily attacked by reagents. Fluorine has no action on it in the cold, but attacks it below a red heat with incandescence and the production of white fumes. Hydrogen is without action on the sulphide at 1200°, and carbon does not reduce it under the influence of an arc from a current of 1000 ampères and 50 volts.

C. H. B.

Compounds of Ferrous Chloride and Nitric Oxide. By V. THOMAS (*Compt. rend.*, 1895, **121**, 204—206).—The three compounds of ferrous chloride and nitric oxide (Abstr., 1895, ii, 271) have no appreciable tension of dissociation at the ordinary temperature either in a vacuum or in a current of a carefully dried, inert gas. Water dissolves the compound, $\text{Fe}_2\text{Cl}_4\cdot 2\text{NO}$, without any evolution of gas, and no gas is evolved if the other two compounds are added to a large proportion of water; but if water is allowed to drop on the solid compounds, gas is liberated in large quantity. Potassium hydroxide or ammonia behaves similarly with all three compounds, and produces a greyish-white precipitate which rapidly becomes bluish-green and, finally, black. There is no liberation of gas, and the liquid contains neither a nitrate nor a nitrite, nor ammonia; the solutions obtained by Gay's methods (Abstr., 1885, 1109), on the other hand, evolve large quantities of a mixture of nitrous oxide and nitrogen. When the black precipitate, produced by alkalis in solutions of the solid compounds, is placed in a vacuum, it gives off a considerable quantity of almost pure nitrogen. If a solution of the compound $\text{Fe}_2\text{Cl}_4\cdot 2\text{NO}$ is precipitated with silver nitrate, there seem to be indications of the formation of silver hyponitrite; but this supposition could not be confirmed, and the phenomena are not shown by the other two compounds. Nitric oxide is only very slowly absorbed by solutions of the compounds $\text{Fe}_2\text{Cl}_4\cdot \text{NO}$ and $5\text{Fe}_2\text{Cl}_4\cdot \text{NO}$, and seems to act as an oxidising agent.

C. H. B.

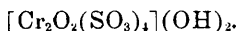
Ammonia and the Chlorides of Iron. By ALFRED S. MILLER (*Amer. Chem. J.*, 1895, **17**, 570—571).—Anhydrous ferric chloride will absorb 6 mols. of ammonia, forming the compound $\text{FeCl}_3\cdot 6\text{NH}_3$ at ordinary temperatures; five mol. are retained in a perfectly dry atmosphere at the ordinary temperature, but at 100° the compound becomes $\text{FeCl}_3\cdot 4\text{NH}_3$. The ammonia compound is not deliquescent, and is insoluble in water, but loses ammonia and chlorine when washed; it dissolves in mineral acids, yielding red solutions. The compound showed a gradual dissociation (*sic*) with formation of ammonium chloride, from 100° to 280°; just below 280°, it was entirely

dissociated. The compound absorbs dry chlorine with a considerable development of heat.

Ferrous chloride absorbs approximately 6 mols. of ammonia at the ordinary temperature, forming a white powder, $\text{FeCl}_2 \cdot 6\text{NH}_3$, which readily oxidises in air. When heated at 100° in hydrogen, the compound became $\text{FeCl}_2 \cdot 2\text{NH}_3$.
A. G. B.

Chromium Sulphate. By ALBERT RECOURA (*Ann. Chim. Phys.*, 1895, [7], 4, 494—527).—This paper is mainly a *résumé* of work previously published elsewhere (compare Abstr., 1891, 1430; 1892, 411 and 783; 1893, ii, 470 and 528; 1894, ii, 382).

It is shown that when a solution of the violet chromium sulphate is heated for some time at 100° , it becomes green, and that the solution then contains free sulphuric acid and a basic salt formed according to the equation $2\text{Cr}_2(\text{SO}_4)_3 + \text{H}_2\text{O} = \text{Cr}_4\text{O}(\text{SO}_4)_5 + \text{H}_2\text{SO}_4$. The salt thus formed is the sulphate of a radicle $[\text{Cr}_4\text{O}(\text{SO}_4)_5](\text{OH})_2$, which the author terms *sulphochromyl hydroxide*. The violet sulphate, $\text{Cr}_2(\text{SO}_4)_3 + 18\text{H}_2\text{O}$, when heated to 90° loses water, and gives the compound $\text{Cr}_2\text{S}_3\text{O}_{12} + 8\text{H}_2\text{O}$, which is neither a sulphate nor yet a chromium salt. The same compound may be obtained from a solution of the violet salt; it is characterised by the ease with which it unites with 1, 2, or 3 mols of sulphuric acid or of a metallic sulphate, thus giving rise to the chromosulphuric acids and the chromosulphates. Under special conditions, this compound can also unite with 5 or 6 mols. of sulphuric acid, yielding compounds with quite distinct constitutions and properties. The latter compounds are much less stable than the chromosulphuric acids; they lose sulphuric acid at 140° , and yield sulphochromic hydroxide,



This is an acid of chromium which is characterised by the insolubility of all its salts.
J. J. S.

Molybdenum Dihydroxychloride. By AD. VANDENBERGHE (*Zeit. anorg. Chem.*, 1895, 10, 47—59).—The author has determined the molecular weight of molybdenum dihydroxychloride by means of the boiling point and freezing point methods with the object of determining its constitution. The compound is prepared by heating molybdic anhydride at 200° in a current of dry hydrogen chloride; it sublimes in lustrous, white crystals, and, when slowly cooled, in beautiful, bright yellow needles, and is very hygroscopic.

The determination of the molecular weight by means of the boiling point method was performed in a modification of Beckmann's apparatus, and the molecular weight calculated from the formula $M = Kp/lt$. With ether and acetone as solvents, the numbers obtained agree with the theoretical value, 217, assuming that the compound is an atomic compound of the constitution $\text{MoO}(\text{OH})_2\text{Cl}_2$, that is, the action of hydrogen chloride on molybdic anhydride is analogous to its action on sulphuric anhydride. With methylic and ethylic alcohols as solvents, a smaller molecular weight was obtained corresponding with that required if the compound is dissociated into its ions, Cl and $\text{MoO}_3\text{H}_2\text{Cl}$.

The determination of the molecular weight by the freezing point method, using anhydrous acetic acid, gave results agreeing with the numbers obtained with methylic alcohol by the boiling point method; with water as the solvent, however, numbers were obtained closely approaching 54.2, which is the number required, assuming that the compound is dissociated into the ions Cl , Cl , H and $\text{O}:\text{Mo}:\text{OH}:\text{O}$.

The author has attempted, without success, to determine the vapour density of the compound; it is already dissociated at 158° and 181° .
E. C. R.

Molybdenum Bronzes. By ALFRED STAVENHAGEN and E. ENGELS (*Ber.*, 1895, 28, 2280—2281).—When acid sodium molybdate, $\text{Na}_6\text{Mo}_2\text{O}_{21}$, is fused and submitted to electrolysis, a substance is formed which crystallises in quadratic prisms of a deep blue colour. It is insoluble in hydrochloric acid, but dissolves in aqua regia and in alkalis. The substance contains 6 per cent. of sodium and 62.7 per cent. of molybdenum, and is looked on by the authors as a sodium molybdenum bronze.
A. H.

Preparation of Tin Tetrachloride in large Quantities. By RICHARD LORENZ (*Zeit. anorg. Chem.*, 1895, 44—46).—Tin tetrachloride is most easily prepared by the action of chlorine on tin at the ordinary temperature. The most suitable apparatus is a tube closed at one end, 5 to 6 cm. wide, and 75 to 100 cm. long, fitted with a condenser and a tube, by means of which dry chlorine can be passed to the bottom of the tube, where it bubbles through a little tin tetrachloride. The tube is filled nearly to the top with granulated tin. $1\frac{1}{2}$ to 2 kilos. of the tetrachloride are easily prepared in about one hour. The product is pure, and boils at 114° .
E. C. R.

Chemistry of the Cyanide Process for the Extraction of Gold from its Ores. By GEORGE A. GOYDER (*Chem. News*, 1895, 72, 80—82, 95—97).—The amount of simple cyanide in a solution containing certain double cyanides, such as the zinc potassium cyanide in the final solution of the cyanide process, cannot be accurately estimated by titration with standard silver nitrate in the presence of a little potassium iodide, because the final reaction is indistinct, and, moreover, an amount of silver nitrate is used up by these double cyanides, which increases continuously with the temperature, with the amount of fresh simple cyanide added, and with the dilution. The author has observed that hydrocyanic acid does not decolorise phenolphthalein, that potassium cyanide is alkaline to it, and that the double cyanides are neutral, and on this has based the following method of testing the final liquors for simple cyanide, which, however, is not applicable in the presence of caustic alkalis or alkali carbonates; alkali hydrogen carbonates do not interfere. 100 c.c. of the solution is titrated with decinormal hydrochloric acid, using 1 c.c. of 0.05 per cent. solution of phenolphthalein as indicator, 1 c.c. of acid = 0.0065 per cent. of potassium cyanide. The estimation of all the cyanides, except the iron, mercury, or copper potassium cyanides, may be effected by the silver method if the solution be

mixed with half its volume of 5 per cent. caustic soda, filtered, and about 15 c.c. of the filtrate taken for titration.

The following are the numbers per cent. obtained from the analysis of the final solution from the treatment of the Mount Torrens ore by the cyanide process. Cu 0.0030, Zn 0.0178, Fe 0.0061, Ca 0.0145, Mg 0.0042, K 0.0609, Na 0.0645, Cl 0.0875, CN 0.0477, SO_3 0.0401, CO_2 0.0333, and traces of Co, Hg, Ag, and Au. Numbers, too, are given showing how the progress of the extraction may be followed by observing the strength of the outflowing solution.

Data are also furnished showing that without further comminution little or no gold can be extracted by potassium cyanide from the tailings. Furthermore, it is shown that hydrocyanic acid in the presence of air, and the double cyanides of zinc and potassium and of copper and potassium exert a solvent action on gold, but that the corresponding mercury salt does not. Allowing one lot of cyanide solution to drain away from the ore undergoing extraction before adding a fresh lot was found to be destructive to the cyanide without commensurate benefit. The destructiveness of ferrous and other soluble metallic salts is commented on.

D. A. L.

Mineralogical Chemistry.

The Crystalline Form of chemically simple Substances. By FRIEDRICH KINNE (*Zeit. physikal. Chem.*, 1895, **16**, 529—545).—Retgers has pointed out that most elements and diatomic compounds, as well as many triatomic compounds, crystallise either in the regular or in the hexagonal system (*Abstr.*, 1894, ii, 348); he has, however, failed to recognise any further relation between this chemical simplicity and the crystalline form. The author finds, however, that such substances belonging to the hexagonal system fall into three groups, each characterised by similarity of crystal angles and habit. (1) The magnesium type with $a : c$ about 1 : 1·6, and of hexagonal symmetry; this group includes zinc oxide, ice, tridymite (SiO_2), greenockite (CdS), niccolite (NiAs), lead iodide, &c. (2) The arsenic type with $a : c$ about 1 : 1·3, and of rhombohedral symmetry; this includes bismuth, sulphur, tellurium, zinc, graphite, millerite (NiS), &c. (3) The quartz type with $a : c$ about 1 : 1·1, and also of rhombohedral symmetry; cinnabar falling in this group. Of elements and simple compounds belonging to the tetragonal system, an α -tin type and a rutile type are distinguished on the same lines. Some less simple compounds and also some pseudo-hexagonal substances can be referred to these types. Retgers's criticism of the author's views (*Zeit. physikal. Chem.*, **14**, 522) are discussed. L. J. S.

Silver Minerals of the Australian Broken Hill Consols Mine. By GEORGE SMITH (*Journ. and Proc. Roy. Soc., N.S.W.*, 1893, **27**, 363—375).—This mine, which is very rich in silver minerals, is where the new mineral willyamite (this vol., ii, 31) was found.

Dyscrasite occurs in large masses, sometimes weighing 23 cwt. and containing 80—83 per cent. of silver; the more common proportions of silver and antimony in this ore are Ag_3Sb , Ag_2Sb , Ag_6Sb , Ag_{12}Sb .

Argentite is rare; a typical impure specimen gave 78 per cent. of silver.

Stephanite occurs only in small quantity, a specimen of sp. gr. 6.23 gave 67.1 per cent. of silver.

Pyrargyrite, amorphous, gave 56.3 per cent. of silver.

Sternbergite occurs with dyscrasite and pyrargyrite, it is of a bronze colour, with a blue tarnish; sp. gr. 4.34; it gave 33.94 Ag, 30.76 Fe, and a little antimony.

Stromeyerite is the principal ore of this mine; it is never crystalline; contains about 30 per cent. of silver, and often a little antimony.

Argentiferous tetrahedrite is also an abundant ore, it usually contains about 20 per cent. of silver; the richer ore (in silver) is lighter in colour and brighter in lustre than the poorer.

Bronziardite is very rare, it occurs with stromeyerite; the purest is crypto-crystalline and resembles argentite; it is encrusted with grey lead carbonate, into which it has been altered; it contains $34\frac{1}{2}$ per cent. of silver.

Antimonial silver chloride; pure silver chloride and bromide are comparatively rare in this mine, the larger masses are always antimonial, of a grey colour and with about 35 per cent. of silver. Some of the masses enclose veins of the ordinary chloride, and patches of dyscrasite, from the latter of which the mineral has probably been derived.

Bournonite is massive and impure, with 5 to 7 per cent. of silver, due to admixture of argentiferous tetrahedrite. A sample of the ore gave

Pb.	Cu.	Sb.	Fe.	Ag.	S.	Insol.	Moisture [by diff.].
29.0	8.9	25.0	3.0	5.7	22.5	3.0	[2.9]

Chlorargyrite gave 73.1 per cent. of silver.

Iodyrite is fairly plentiful, always occurring in limonite.

Galena contains varying amounts of silver, and has 65 to 83 per cent. of lead; it is often altered to anglesite, this being afterwards altered to cerussite. Also Johnstoneite?

Cerussite contains about 60 per cent. of lead; silver is also present.

The vein stuff of the mine is calcite and siderite, which in the upper parts is replaced by limonite. Copper ores only occur in small quantity. About 50 minerals are mentioned or shortly described, amongst them being vanadinite, volgerite, and native sulphur.

L. J. S.

Lorandite, a new Thallium Mineral. By JÓZSEF A. KRENNER (*Math. és Természett. Ertesítő*, 1894, 12, 471, and *Ber. aus Ung.*, 1895; 12, 262).—This new and rare mineral occurs as tabular or short prismatic, mono-symmetric crystals on realgar at Allchar, Macedonia; the colour is cochineal- to kermesite-red, and the crystals are transparent, and can be bent like selenite. Analysis gave

S.	As (calc. from loss).	Tl.
19.02	(21.47)	59.51

This agrees with the formula TlAsS_2 .

L. J. S.

Composition of Kermesite. By HENRI BAUBIGNY (*Compt. rend.*, 1894, 119, 737—740).—Partial analysis gave Sb 75·13, S 20·04 per cent. This agrees with the formula Sb_2OS_2 , or $2\text{Sb}_2\text{S}_3, \text{Sb}_2\text{O}_3$, which was deduced from the early analysis of H. Rose, the only one that has been previously made of the mineral. Tartaric acid solution had practically no action on the mineral. L. J. S.

Willyamite, a New Mineral from Broken Hill, N.S.W.—By EDWARD F. PITTMAN (*Zeit. Kryst. Min.*, 1895, 25, 291; from *Journ. and Proc. Roy. Soc., N.S.W.*, 1893, 27, 366—368).—This new mineral was found with dyscrasite in a calcite and siderite vein. The crystal system is regular, and there is a perfect cubic cleavage; fracture uneven. Colour between tin-white and steel-grey; lustre metallic; streak greyish-black. $H = 5\frac{1}{2}$; sp. gr. 6·87. Analysis by J. C. H. Mingaye, gave

	Sb.	Co.	Ni.	S.	Total.
I.	56·85	13·92	13·38	15·64	99·79
II.	56·71	13·84	13·44	15·92	99·91

There are also traces of iron, copper, and lead. The formula is $\text{CoS}_2, \text{NiS}_2, \text{CoSb}_2, \text{NiSb}_2$, which corresponds with ullmannite in which half the nickel is replaced by cobalt. L. J. S.

Calaverite from Cripple Creek, Colorado. By WILLIAM F. HILLEBRAND (*Amer. J. Sci.*, 1895, [3], 50, 128—131).—Tellurium has been previously known to occur in the ores of this district, partly in combination with gold as gold-tellurium (sylvanite). Analyses of the present mineral were made on material from three mines, namely, Prince Albert mine, I; Raven mine, II; and C.O.D. mine, III.

	Te.	Au.	Ag.	Insol.	Fe_2O_3 .	Fe.	S.	Total.
I.	57·27	38·95	3·21	0·33	0·12	—	—	99·88
II.	47·69	33·93	1·47	5·80	—	5·41	6·17	100·47
III.	53·89	39·31	0·85	0·91	—	1·67	1·58	—

In III also Mn, 0·23; Ca, 0·51; Mg, 0·10; O, F, and soluble silica by difference, 0·95. These analyses, after deducting gangue, reduce to the formula $(\text{Au}, \text{Ag})\text{Te}_2$; the amount of silver, in analysis I, agrees with that in Genth's analyses, but is less in II and III. The mineral is of a pale bronze-yellow colour, the powder being greenish-grey; sp. gr. 9·00. The imperfect and deeply striated crystals of prismatic habit seem, according to Penfield, to be asymmetric, but with angles and axial ratios near to sylvanite. L. J. S.

Nantokite from New South Wales. By ARCHIBALD LIVERSIDGE (*Min. Mag.*, 1894, 10, 326—327).—This mineral was found associated with cuprite, native copper, cerussite and quartz, at the Broken Hill South mine; when freshly fractured, it is colourless and transparent with a highly vitreous lustre. On exposure, the mineral soon effloresces and becomes green. Analysis, by J. O. Armstrong and A. D. Carmichael, gave

Cu.	Cl.	Total.	Sp. gr.
64.28	35.82	100.10	4.1

The mineral is soluble in ammonia, hydrochloric acid, and in a solution of sodium chloride; when heated with water, cuprous oxide is deposited, and some copper goes into solution as cupric chloride.

L. J. S.

Artificial Percylite. By CHARLES FRIEDEL (*Bull. Soc. fran. Min.*, 1892, 15, 96—101).—By the prolonged action of copper chloride solution on lead hydroxide, a blue, crystalline powder was formed; this consists of strongly birefringent tetragonal octahedra, having the characters of the tetragonal variety of boleite (Abstr., 1892, i, 123), and also, in much smaller quantity, of cubic crystals corresponding with the cubic variety of boleite. Analysis of the material agreed with the formula $\text{PbCl}\cdot\text{OH}, \text{CuCl}\cdot\text{OH}$, and the name percyllite is here given (apparently to both kinds of crystals), to distinguish it from the silver-holding boleite. [The first kind of crystals have since been named *cumengeite* by Mallard, Abstr., 1895, ii, 115, and 1893, ii, 417]. Phosgenite was also formed by the above reaction.

L. J. S.

Artificial Boleite. By CHARLES FRIEDEL (*Bull. Soc. fran. Min.*, 1894, 17, 6—8).—A mixture of lead and silver hydroxides, in the proportion they exist in boleite, with some clay, was acted on by copper chloride solution for several months; the action was much slower than when cumengeite was formed (preceding Abstr.). In the clay were found blue cubic crystals which were built up exactly like certain crystals of boleite; having an isotropic cubic nucleus, surrounded by six truncated tetragonal pyramids. The crystals were too small in quantity and too impure for analysis, but they certainly differ from those formed without the intervention of silver.

L. J. S.

Boleite from New South Wales. By ARCHIBALD LIVERSIDGE (*Journ. and Proc. Roy. Soc. N.S.W.*, 1894, 28, 94—96).—This mineral occurs at the Broken Hill South mine with hæmatite and quartz; it is of an indigo-blue colour with a strong vitreous lustre, and is found as cubes with a nearly perfect cubic cleavage. Analysis by Carmichael and Armstrong gave

Ag.	Pb.	Cu.	Cl.	O (calc.).	H ₂ O (calc.).	Total.	Sp. gr.
8.25	47.20	19.20	13.50	[6.10]	[5.44]	99.69	5.02

This agrees closely with the analysis of Mallard and Cumenge (Abstr., 1892, i, 123). Liversidge determines the water directly as 6.39 per cent.; this may be a little too high.

L. J. S.

Rubies of Burma. By C. BARRINGTON BROWN and JOHN W. JUDD (*Proc. Roy. Soc.*, 1895, 57, 387—394).—The famous ruby district of Upper Burma is situated 90 miles N.N.E. of Mandalay, the principal mining centre being Mogok. The gneissic rocks of the district are of intermediate chemical composition, including biotite-gneiss, biotite-granulite and rarely biotite-schist; interfoliated with these are more acid rocks, such as pegmatites, quartzites &c., also

more basic rocks, such as pyroxene-gneiss &c., these passing into ultra-basic pyroxenites, and thirdly bands of crystalline limestone. In the acid rocks, tourmaline occurs, as in the adjacent rubellite district of Nyoungouk; the basic rocks are rich in garnet, and in the limestone corundum and spinel of various colours occur. The limestones are more closely associated with the basic and ultra-basic rocks, which contain crystals of calcite, and, as the amount of calcite increases, they graduate into the limestones; it being supposed that the limestones have been derived by the alteration of the basic felspars (anorthite) of the basic rocks. The hydrated aluminium silicates, liberated by the same alteration, having in the first place given rise to hydrated aluminium oxides, which are afterwards converted into anhydrous alumina. In the limestones are also found numerous other minerals, such as phlogopite, graphite, pyrrhotite, felspars (moonstone), amphiboles, pyroxenes, lapis lazuli &c.

The subsequent alteration of the rubies is seen as an inner zone of diaspore passing outwards into various hydrous aluminium silicates—margarite, vermiculite, mica, kaolinite &c.; these changes taking place along the primary and secondary solution planes, or planes of chemical weakness, of corundum (Judd, *Min. Mag.*, 1895, **11**, 49).

L. J. S.

Cerussite coated with Galena; Manganite and Chloritoid from Michigan; Apatite and Hessonite in Pegmatite. By WILLIAM H. HOBBS (*Amer. J. Sci.*, 1895, [3], **50**, 121—128).—*Cerussite* in twinned, prismatic crystals, from near Missoula, Montana, was partially coated with an extremely thin, bright film having a metallic lustre. Analysis gave

PbO.	CO ₂ .	$\text{Fe}_2\text{O}_3, \text{Al}_2\text{O}_3$.	SiO ₂ .	S.	Total.
80.83	15.51	0.55	2.15	trace	99.04

The trace of sulphur and excess of lead indicate that the film consists of galena. As this film is only found on the cerussite, and not on the accompanying minerals, it may be considered to be due to the alteration of the cerussite, probably by the action of hydrogen sulphide. From the parts of the crystals, so coated, good measurements of the angles were obtained.

Manganite, from Lucy Mine, Negaunee, Michigan, gave on analysis

Mn.	H ₂ O.	BaCO ₃ , CaCO ₃ .	MgCO ₃ .	O (calc.).	Total.
60.29	10.10	0.58	2.98	26.35	100.30

The crystals are simple in form, but the habit varies slightly according as they are associated with barytes or not. The barytes is described.

Chloritoid, as large porphyritic crystals, occurs in blocks of phyllitic schist on the south shore of Michigamme Lake, Michigan; in the rock also occur colourless mica, biotite, tourmaline, magnetite, and some small blades of chloritoid. The chloritoid crystals, sometimes 6 cm. or more across, are hexagonal in outline and tabular parallel to the base, and are frequently twinned. The analysis, which was made on a crystal enclosing magnetite, this being sur-

rounded by a zone of quartz, is nearly the same as that of the masonite of Natic, Rhode Island.

SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	FeO.	MgO.	CaO.	H ₂ O.	P ₂ O ₅ .	Total.
35.52	23.53	5.85	22.38	0.76	1.38	5.94	trace	101.36

From the optical characters, the crystals seem to be mono-symmetric or asymmetric, with a close approach to the former.

Apatite and Hessonite occur in the pegmatite veins cutting the gneiss about Canaan, Conn., along with other crystallised minerals, such as white feldspar and muscovite in large crystals, biotite and tourmaline. The cinnamon-coloured garnet is sometimes intergrown with feldspar, producing a structure resembling graphic granite. The apatite is green in colour.

L. J. S.

Analysis of Monazite. By ALBERT THORPE (*Chem. News*, 1895, 72, 32).—Analysis of monazite from North Carolina gave

P ₂ O ₅ .	La ₂ O ₃ .	Ce ₂ O ₃ .	ThO ₂ .	SnO ₂ .	MnO.	CaO.	Total.
28.43	23.62	25.98	18.01	1.62	1.33	0.91	99.90

L. J. S.

Evansite from Tasmania. By HENRY G. SMITH (*Journ. and Proc. Roy. Soc., N.S.W.*, 1893, 27, 382—383).—This mineral occurs at Mount Zeehan, as small, globular excrescences, which are colourless and of a vitreous lustre, or milky white and slightly opalescent. Brittle; H = 4; sp. gr. 1.842. When heated, it decrepitates, and gives off water, which, in being alkaline (probably due to sodium), differs from the original evansite. Analysis gave

H ₂ O.	Al ₂ O ₃ .	P ₂ O ₅ .	Total.
41.266	40.186	18.114 (mean of 17.996 and 18.232)	99.566

This agrees with the usual formula 3Al₂O₃.P₂O₅.18H₂O. The perfectly glassy beads contain neither fluorine, silicon, nor iron, but the white, opaque, cellular portions are very siliceous.

L. J. S.

A Bed of Aluminium and Potassium Phosphates in Algeria. By ADOLPHE CARNOT (*Compt. rend.*, 1895, 121, 151—155).—The floor of a stalactitic cavern near Oran, in Algeria, is covered with a deposit, from 1 to 3 metres thick, of a brownish-red phosphatic earth, with white and variegated veins and spongy masses. The cavern and the deposit contain no bones of vertebrata. The white matter consists chiefly of aluminium phosphate mixed with a variable proportion of silica, and sometimes of calcium phosphate; when red, it contains ferric oxide, and, when black, manganese oxide or cobalt oxide. The light, rounded, unctuous, agglomerated masses show no traces of crystalline structure, and are to a large extent soluble in dilute acids and in ammonium citrate solution. One specimen had the composition P₂O₅ 35.17, Al₂O₃ 18.18, K₂O 5.80, NH₃ 0.48, CaO 0.31, SiO₂ 11.60, loss at 100° 13.40, loss at 100—180° 10.55, loss at 180° to a red heat 4.35; MgO, F, Cl, SO₃, traces. Total = 99.84. If the aluminium phosphate is supposed to be the normal salt, the ratio of the remaining phosphoric acid to the other bases is intermediate between that

of monometallic and bimetallic phosphates, and the aqueous solution of the phosphates is neutral to both methyl-orange and phenolphthaleïn. The phosphate does not belong to the same class as Gautier's *minervite* (Abstr., 1893, ii, 536, 577), and the author does not assign to it any definite formula. It is most probable, however, that the deposit has been formed by the infiltration of water containing ammonium phosphate, &c., derived from the oxidation of organic matter and phosphates of animal or vegetable origin, and also alumina derived from minerals (*loc. cit.*). C. H. B.

Retzian. By S. A. HJALMAR SJÖGREN (*Bull. Geol. Inst., Upsala*, 1894, 2, 54—59).—This new arsenate occurs as orthorhombic crystals in the cavities of the manganiferous limestone of the Moss mine, Nordmark, Sweden. It is of a chestnut- to chocolate-brown colour; lustre vitreous, approaching to greasy; subtranslucent. There is no cleavage. Pleochroism strong. Sp. gr. 4.15. The analysis is incomplete owing to lack of material; a constituent (amounting to 10.3 per cent.), separated from the manganese precipitate, not having been identified.

As ₂ O ₅ .	PbO.	FeO.	MnO.	CaO.	MgO.	SiO ₂ .	H ₂ O.	Insol.
24.4	0.2	1.7	30.2	19.2	2.7	0.5	8.4	4.3

The mineral is thus closely related to other hydrous manganese arsenates (allactite, synadelphite, diadelphite, hæmafibrite) from the same mine, and to flinkite from the Harstig mine, Sweden; none of these, however, contain any calcium, and some of them contain Mn₂O₃.

L. J. S.

Artificial Gypsum. By ALEXANDRE GORGEU (*Bull. Soc. fran. Min.*, 1894, 17, 8—9).—A flask containing calcium sulphite and filled with an aqueous solution of sulphurous acid was corked up; after several years a part of the sulphite was oxidised, and beneath the deposit at the bottom of the flask were thin crystals 1—3 cm. long. These at the attached ends were opaque owing to enclosed sulphite, but the transparent portions of the crystals contained no sulphurous acid, and on ignition lost 20.8 per cent. of water; they showed the usual cleavage, twinning &c. of gypsum.

L. J. S.

Leadhillite Pseudomorphs in Missouri. By WARREN M. FOOTE (*Amer. J. Sci.*, 1895, [3], 50, 99—100).—Leadhillite has recently been described from Granby, Mo., by Pirsson and Wells, (Abstr., 1894, ii, 458). The pseudomorphs with the form of scalenohedra of calcite consist often of cerussite, but sometimes of leadhillite, either as epimorphs or replacing the whole of the calcite. Pure white leadhillite also occurs in the form of cubes after galena; but in most cases the galena is represented by crusts and hollow forms of a grey amorphous material, this consisting of leadhillite containing some galena. Scattered through some crystals of leadhillite are to be seen the bright cleavages of galena.

L. J. S.

Kauaiite, a new mineral from Hawaii. By EDWARD GOLDSMITH (*Proc. Acad. Nat. Sci., Philadelphia*, 1894, 105—107).—This volcanic product is white or faint cream coloured, and is dull and powdery

closely resembling chalk in appearance. Under the microscope, it is seen to consist of granules all of about the same size, and it is pale blue by transmittent light; sp. gr. 2.566. When heated, it decrepitates slightly and becomes dark grey, giving off an oily substance and acid water; it becomes intensely incandescent before the blowpipe. It is soluble in acids only after ignition, but is dissolved by caustic alkali.

Eliminating about 5.94 per cent. of carbonaceous matter, the results of the analysis are

Al_2O_3 .	K_2O .	Na_2O .	H_2O .	SO_3 .
39.79	7.37	1.72	33.56	17.55

This gives the formula $2\text{Al}_2\text{O}_3 \cdot 3(\text{K}, \text{Na}, \text{H})_2\text{O} \cdot \text{SO}_3$. This highly basic sulphate is distinguished from others in being insoluble in acids.

L. J. S.

Melanterite containing Zinc. By LÉOPOLD MICHEL (*Zeit. Kryst. Min.*, 1895, **25**, 316; from *Bull. Soc. fran. Min.*, 1893, **16**, 204).—Massive, pale green concretions of melanterite from Laurion, Greece, gave on analysis

SO_3 .	FeO .	ZnO .	H_2O .	Total.
28.85	17.74	8.92	44.21	99.72

Formula $(\text{Fe}, \text{Zn})\text{SO}_4 \cdot 7\text{H}_2\text{O}$. Sp. gr. 1.95.

L. J. S.

Artificial Powellite. By LÉOPOLD MICHEL (*Bull. Soc. fran. Min.*, 1894, **17**, 612—614).—On heating to a high temperature a mixture of six parts of sodium molybdate, one of sodium tungstate, three of calcium chloride and two of sodium chloride, translucent, milky-white crystals of powellite were formed; these have the form of tetragonal octahedra, and are about 2 mm. in diameter; they have an adamantine lustre and are optically positive. Analysis gave

MoO_3 .	WO_3 .	Ca.	Total.	Sp. gr.
62.37	10.23	26.41	99.01	4.61

L. J. S.

Pimelite and Asbeferrite. By EDWARD GOLDSMITH (*Zeit. Kryst. Min.*, 1895, **25**, 281; from *Proc. Acad. Nat. Sci., Philadelphia*, 1893, 174—175).—*Pimelite* occurs as a soft, greasy, very finely micaceous mineral of apple-green colour at Radnor, Delaware Co., Penn.; sp. gr. 2.596; given as probably mono-symmetric. It is decomposed by boiling hydrochloric acid, leaving 31.1 per cent. of insoluble sandy material. The soluble part, which is supposed to be pimelite, gave analysis I, from which the formula $(\text{Mg}, \text{Ni}, \text{H}_2)\text{O} \cdot \text{SiO}_2$ is derived.

SiO_2 .	MgO .	NiO .	H_2O .	Fe_2O_3 .	CaO .	Mn.
I. 45.93	34.44	7.69	11.68	—	—	—
II. 48.45	6.23	—	—	33.90	11.80	trace

Asbeferrite occurs as a secondary product, mixed with pyrites and on calcite, at the iron mine near the Falls of French Creek, Chester Co., Penn.; it is of a greyish-green colour, and consists of fine fibres matted together. Analysis II differs considerably from Igelström's analysis of asbeferrite. On heating, the mineral becomes a rusty colour.

L. J. S.

Felspar of the Acmite-trachyte of the Crazy Mountains, Montana. By T. E. WOLFF and RALPH S. TARR (*Zeit. Kryst. Min.*, 1895, 25, 281; from *Bull. Mus. Comp. Zool., Harvard Coll.*, 1893, 16, No. 12).—The acmite-trachyte of this locality occurs as dykes, and contains felspar, ægirine, and sodalite in a ground mass of felspar, ægirine, and either nepheline or analcite. The optical extinction angles and the composition of the large felspar crystals point to soda-microcline or anorthoclase; analysis gave

SiO ₂ .	Al ₂ O ₃ .	CaO.	SrO.	BaO.	K ₂ O.	Na ₂ O.	Loss (H ₂ O).	Total.
62·31	22·63	0·63	0·57	0·77	4·79	7·68	0·72	100·10

L. J. S.

Analyses of Sodalite from New Localities. By L. McI. LUQUER and G. J. VOLCKENING (*Amer. J. Sci.*, 1895, [3], 49, 465—466).—Under I is given the analysis of massive, cobalt-blue sodalite from the Laurentian system at Hastings Co., Ontario, Canada; the mineral shows a very distinct cleavage, and in thin section there are a few cloudy patches due to decomposition. A similar specimen from the Urals gave analysis II; in thin section a very perfect cleavage is seen, with commencing decomposition along the cleavage cracks. Another similar specimen from Congo State, Africa (III), showed in section only an imperfect cleavage and some decomposition; it is associated with limonite and decomposed felspar, and is the only known African occurrence of the mineral.

	SiO ₂ .	Al ₂ O ₃ .	CaO.	Na ₂ O.	K ₂ O.	Cl.	Total.	O = Cl.	Sp.gr.
I.	37·34	31·25	0·38	25·01	0·74	6·79	101·51	1·53	2·303
II.	37·28	31·60	0·46	24·74	0·93	6·65	101·66	1·50	2·328
III.	37·85	30·87	0·51	25·43	0·22	6·46	101·34	1·46	2·363

L. J. S.

Constitution of the Lithia Micas. By FRANK W. CLARKE (*J. Amer. Chem. Soc.*, 1893, 15, 245—250).—The micas have been considered by Clarke to be derivatives of the normal aluminium orthosilicate, Al₄(SiO₄)₃ (Abstr., 1890, 460); in the lithia micas, however, there is an oxygen ratio lower than that of the orthosilicate, and they are further characterised by the presence of fluorine. The lower oxygen ratio is explained by the partial replacement of SiO₄ by Si₃O₈, and the fluorine, which was previously explained by the presence of the group AlF₂ among the components of R', is now explained by assuming that the clintonite type, R'' <math display="block">\begin{smallmatrix} & O \\ & \diagup \quad \diagdown \\ R'' & & O \end{smallmatrix} > Al \cdot SiO_4 R'_3, is replaced by the molecule AlF₂·SiO₄R'₃.

In polyolithionite, SiO₄ is entirely replaced by Si₃O₈, and Lorenzen's analyses may be represented by 5(AlF₂·Si₃O₈Li₃) + Al(Si₃O₈)₃(Na₂K)₃. All the variations in composition of the lepidolites proper may be explained by the supposition that these micas are mixtures of two typical molecules, namely, AlF₂·Si₃O₈R'₃, where R' is principally lithium, and a muscovite molecule, Al₃(SiO₄)₃R'₃, in which R'₃ may be K₂H or KH₂; some peculiarities are explained by a small admixture of the molecule AlF₂·Si₃O₈Al. Cookeite, which appears to be the

vermiculite of the lepidolite series, has the fluorine replaced by hydroxyl, and we have a mixture of the three molecules, $\text{Al}(\text{OH})_2\cdot\text{SiO}_4\text{Li}_3$, $\text{Al}(\text{OH})_2\cdot\text{SiO}_4\text{H}_3$, and $\text{Al}(\text{OH})_2\cdot\text{SiO}_4\text{Al}$.

In the iron-lithia micas, zinnwaldite and cryophyllite, the case is more complicated, as the iron may belong to the molecule $\text{AlF}_2\cdot\text{Si}_3\text{O}_8\text{Fe}'\text{R}'$, or to the biotite molecule $\text{Al}_2(\text{SiO}_4)_3\text{Fe}''\text{R}''_2$. Some zinnwaldites may be represented by mixtures of $\text{AlF}_2\cdot\text{Si}_3\text{O}_8\text{FeLi}$ and $\text{Al}_3(\text{SiO}_4)_3\text{K}_3$, whilst cryophyllite is most easily represented by $\text{Al}_3\text{X}_3\text{KH}_2 + 2(\text{Al}_2\text{X}_3\text{Fe}_2\text{H}_2) + 3(\text{AlF}_2\cdot\text{XK}_3) + 4(\text{AlF}_2\cdot\text{XLi}_3)$, in which X represents SiO_4 and Si_3O_8 in the ratio 1 : 3. L. J. S.

Garnet from California. By FRANK W. CLARKE (*Amer. J. Sci.*, 1895, [3], 50, 76—77).—A water-worn pebble, found 40 miles south of Los Angeles, closely resembled jade in being highly polished, very compact, and of an apple-green colour; analysis gave

SiO_2 .	Al_2O_3 .	Fe_2O_3 .	FeO .	CaO .	MgO .	Alkalis.	Ignition.	Total.
37·54	22·84	0·79	0·26	36·66	0·44	0·13	1·74	100·40

Also traces of TiO_2 , P_2O_5 and CO_2 ; sp. gr. 3·485. Hydrochloric acid extracts about 16 per cent. of Al_2O_3 , and about 20 per cent. of CaO . As a grossular garnet simulating jade, it is of interest. L. J. S.

Almandine Garnet from the Hawkesbury Sandstone, Sydney, N.S.W. By HENRY G. SMITH (*Journ. and Proc. Roy. Soc., N.S.W.*, 1894, 28, 47—50).—"Precious Garnet" occurs as small, irregular, reddish particles in a conglomerate (probably derived from granite) in the Hawkesbury sandstone. The colour is light, but sometimes deep red or purple; the mineral is isotropic, and shows a distinct cubical cleavage; sp. gr. 3·902. Analysis gave

SiO_2 .	Al_2O_3 .	Fe_2O_3 .	FeO .	MgO .	Mn.	Total.
38·704	21·795	2·168	27·750	9·725	trace	100·142

The sesquioxides are a little too high for the garnet formula.

L. J. S.

Analysis of Anorthite from Raymond, Maine. By WILLIAM H. MELVILLE (*Bull. U.S. Geol. Survey*, 1893, No. 113, 110).—White crystals associated with idocrase, cinnamon garnet, pyroxene, and scapolite; gave, on analysis,

SiO_2 .	Al_2O_3 .	Fe_2O_3 .	CaO .	MgO .	K_2O .	Na_2O .	H_2O (at 100°).	Loss on ignition.	Total.
43·13	30·95	1·04	19·71	0·31	1·29	0·69	0·22	2·80	100·14

Also traces of FeO , MnO and Li_2O .

L. J. S.

Analysis of Prehnite from Fassa, Tyrol. By EDWARD A. SCHNEIDER (*Bull. U.S. Geol. Survey*, 1893, No. 113, 112).—This analysis was made in connection with the experiments noticed in the Abstract, 1892, 772.

SiO_2 .	Al_2O_3 .	Fe_2O_3 .	CaO .	H_2O (at 105°).	H_2O (at 250—300°).	Loss on ignition.	Total.
43·32	25·50	trace	26·49	0·17	0·14	4·70	100·32

L. J. S.

Analyses of Biotite and Hornblende from Japan. By BUNDJIRŌ KOTŌ (*Zeit. Kryst. Min.*, 1895, 25, 287; from *Journ. Coll. Sci., Imp. Univ., Tōkyō*, 1893, 5, 225).—These minerals, from the amphibole- and biotite-granites, are described in a paper on the Archæan formation of the Abukuma Plateau. The biotite (I) is dark brown, and almost opaque, and is nearly optically uniaxial; Hida's analysis shows it to be lepidomelane. The hornblende (II) is bluish-green in colour, and with only feeble pleochroism.

	SiO ₂ .	Al ₂ O ₃ .	FeO.	CaO.	MgO.	Mn ₃ O ₄ .	Na ₂ O.	K ₂ O.	Total.
I.	36·60	17·05	21·29	trace	10·36	0·70	5·39	8·49	99·88
II.	45·61	4·47	8·92	26·40	11·44	—	2·26	0·79	99·89

L. J. S.

Analyses of Ottrelite, Pyroxene, Garnet, Epidote, Scolecite, and Xenotime. By L. G. EAKINS (*Bull. U.S. Geol. Survey*, 1893, No. 113, 111—112).—Ottrelite (I) from the Ottrelite-phyllite rock occurring at Liberty, Frederick Co., Maryland. Pyroxene (II), Garnet (III), Epidote (IV), Scolecite (V), all from Italian Peak, Gunnison Co., Colorado.

	I.	II.	III.	IV.	V.
SiO ₂	23·40	47·53	36·88	37·22	45·90
TiO ₂	1·19	—	—	—	—
Al ₂ O ₃	39·31	9·88	10·34	24·09	26·51
Fe ₂ O ₃	5·14	1·79	17·51	12·80	—
FeO	21·94	0·91	—	0·79	—
MnO	trace	trace	—	0·11	—
CaO	trace	25·46	34·85	23·36	14·17
MgO	2·18	14·43	0·43	trace	trace
Na ₂ O	0·20	trace	trace	0·06	trace
K ₂ O	0·20	—	—	—	—
H ₂ O	6·81	0·30	0·21	1·61	13·79
F	—	—	—	0·06	—
P ₂ O ₅	trace	—	—	—	—
	100·37	100·30	100·22	100·10	100·37
Sp. gr.	—	3·312	3·721	3·452	2·247

Xenotime from the gold washings at Brindletown, North Carolina (*Abstr.*, 1894, ii, 54); gave, on analysis,

	SiO ₂ .	ZrO ₂ .	UO ₂ .	ThO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	(LaDi) ₂ O ₃ .	(YEr) ₂ O ₃ (mol. wt. 260).
Green....	3·46	1·95	4·13	trace	0·77	0·65	0·93	56·81
Brown...	3·56	2·19	1·73	trace	1·57	2·79	0·77	55·43
	CaO.	P ₂ O ₅ .	F.	H ₂ O.	Total.	Sp. gr.		
	0·21	30·31	0·06	0·57	99·85	4·68		
	0·19	29·78	0·56	1·49	100·06	4·46		

L. J. S.

Analyses of Nickel-iron sulphide, Bauxite, Felspars, and Piedmontite. By WILLIAM F. HILLEBRAND (*Bull. U.S. Geol. Survey*,

1893, No. 113, 109—111).—*A nickel-iron sulphide* from Worthington mine, 25 miles west of Sudbury, Ontario. Greyish with a cast of yellow. Not pyrrhotite; possibly a mixture of pyrites and polydymite.

Fe.	Ni.	Mn.	S.	SO ₃ .	CO ₂ (calc. from CaO).	CaO.
38·36	4·57	0·10	45·11	0·95	1·49	1·91
		MgO.	Insol.	H ₂ O (at 100°).	Total.	
		0·41	4·80	0·55	98·25	

Bauxite from near Jacksonville, Calhoun Co., Alabama; I, red, II, white. Lime, magnesia and alkalis were not looked for.

SiO ₂ .	TiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	P ₂ O ₅ .	H ₂ O (at 100°).	H ₂ O (on ignition).	Total.
I. 10·25	2·53	41·00	25·25	trace	0·65	20·43	100·11
II. 21·08	2·52	48·92	2·14	trace	0·45	23·41	98·52

Felspars from the pegmatite veins in the gneiss at Jones' Falls, Baltimore, Maryland; I, white albite, composition Ab₄An₁; II, flesh coloured microcline; III, greenish microcline. These are described in *Johns Hopkins Univ. Circulars*, 1893, 12, 97.

SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	FeO.	CaO.	BaO.	MgO.	K ₂ O.	Na ₂ O.
I. 63·72	22·26	trace		3·58	—	0·06	0·76	8·98
II. 65·06	18·41	trace		0·26	0·13	0·04	14·30	1·60
III. 68·48	16·11	0·20	0·17	0·23	0·05	0·03	12·99	1·27
		H ₂ O (at 100°).	H ₂ O (above 100°).	Total.				
		I. 0·09	0·43	99·88				
		II. 0·04	0·26	100·10				
		III. 0·06	0·26	99·85				

All these contain traces of strontium and lithium; in III quartz was not wholly separated.

Piedmontite from rhyolite at Pine mountain, near Monterey station, Maryland; contains a little admixed quartz.

SiO ₂ .	Al ₂ O ₃ .	Ce ₂ O ₃ .	X ₂ O ₃ . (Mol. wt. 295).	Fe ₂ O ₃ .	Mn ₂ O ₃ .	MnO.	PbO.
47·37	18·55	0·75	1·28	4·02	6·85	1·92	0·14

CuO.	CaO.	MgO.	K ₂ O.	Na ₂ O.	Li ₂ O.	H ₂ O (at 100°).	H ₂ O (above 100°).	P ₂ O ₅ .	Total.
0·11	15·82	0·25	0·68	0·23	trace	0·14	1·94	trace	100·05
L. J. S.									

Basalt from Bondi, N.S.W. By J. MILNE CURRAN (*Journ. and Proc. Roy. Soc., N.S.W.*, 1894, 28, 217—231).—This rock, which contains olivine, augite, plagioclase, magnetite, sodalite, apatite, mica and a glassy base, is easily gelatinised by hydrochloric acid, 56·4 per cent. being soluble, and the solution on evaporation deposits numerous cubes of sodium chloride. Calculated from the chlorine,

the amount of sodalite in the rock is 8 per cent., this requires 1.92 per cent. of soda; as the other minerals (felspars) containing sodium are only present in small quantity, some of the soda is supposed to exist in the glassy base. The fresh rock, of sp. gr. 2.94, gave analysis I, and the decomposed rock II.

	SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	FeO.	CaO.	MgO.	Na ₂ O.	K ₂ O.	TiO ₂ .
I.	43.5	14.60	5.40	8.28	8.70	6.16	7.38	2.95	0.10
II.	42.0	40.2	trace	—	nil	nil	4.4	1.6	—
			Cl.	H ₂ O.	Total.				
			I. 0.37	2.50	99.90				
			II. —	12.00	100.2				

I contains also traces of phosphoric acid, and I and II traces of chromic oxide.

L. J. S.

Analyses of Leucite-basalt from Vesuvius. By ALBERT THORPE (*Chem. News*, 1895, **72**, 53).—Analyses of leucite-basalt, from Vesuvius, gave

	SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	FeO.	MnO.	CaO.	MgO.	K ₂ O.
I.	47.23	18.23	4.21	4.49	1.36	8.63	4.68	8.00
II.	47.32	18.00	4.23	4.31	1.42	8.51	5.03	7.92
			Na ₂ O.	TiO ₂ .	P ₂ O ₅ .	Total.		
			I. 2.63	0.23	0.31	100.00		
			II. 2.70	0.36	0.20	100.00		

The sp. gr. of the rock varied from 2.653 to 2.721.

L. J. S.

A Tempered Steel Meteorite. By EDWARD GOLDSMITH (*Proc. Acad. Nat. Sci., Philadelphia*, 1893, 373—376).—This meteorite, weighing 267 lbs., was brought from near Godhaven, Disko Island, Greenland, by the Peary Expedition of 1891; when received it appeared quite fresh, but it soon became cracked and fell to pieces. These pieces were easily separated into hard metallic granules (73.8 per cent. of the whole) and a magnetic powder. The granules were extremely hard and difficult to cut (no diamond was found), but on being heated and slowly cooled, they became soft, hence the above title to the paper; their composition is given as

Fe.	Ni.	Troilite.	Magnetite.	Silicate.	Sp. gr.
66.79	2.32	0.52	25.96	4.41	6.14

Traces of carbon, phosphorus and chromium were found, but neither copper nor cobalt, which are found in the Disko terrestrial iron, together with more carbon than here. The composition of the powder is given as

Fe.	NiO.	Fe ₂ O ₃ .	Fe ₃ O ₄ .2SO ₃ .	Silicate.	H ₂ O.	Sp. gr.
25.58	0.31	56.30	4.28	10.10	3.43	4.73

The "Fe₃O₄.2SO₃" is called "magnetic sulphate," as the whole of the powder is stated to be magnetic.

L. J. S.

Occurrence of Fluorine in certain Mineral Waters. By JOSÉ CASARES (*Zeit. anal. Chem.*, 1895, **34**, 546—548).—The sulphuretted mineral waters of Lugo and Guitiriz (Galicia, Spain) contain so much fluorine that it can readily be detected in the residue of 500 c.c. of the water. Quantitative estimations in the Guitiriz water gave, by Fresenius's method, 0·02344, 0·02806, and 0·02277 gram of sodium fluoride per litre; by Carnot's method (*Abstr.*, 1892, 911), 0·0268 gram. A single estimation in the Lugo water showed 0·0249 gram per litre. The author inclines to the belief that the presence of fluorides in mineral waters is more general than is commonly supposed.

M. J. S.

Physiological Chemistry.

Cutaneous Respiration in the Frog. By E. WAYMOUTH REID and FREDERICK J. HAMBLY (*J. Physiol.*, 1895, **18**, 411—424).—The vital or secretory activity of the epithelium lining the air passages has been recently called on to account for some of the phenomena of respiration. The present research deals with this question in connection with the skin of the frog, which in that animal forms an important coadjutor to the lungs. The apparatus and method used are described at length: the principle of the method is, that the skin just removed from the animal is used as a diaphragm, across which the amount of gases passed is estimated. The amount of carbonic anhydride which passes through the skin, from the inner to the outer surface, is practically the same as that which passes in the reverse direction. There is thus no evidence of secretory activity.

W. D. H.

Action of Mustard and Pepper on Digestion. By GOTTLIEB (*Exp. Stat. Record*, 1895, **7**, 148—149; from *Verhandl. Natur. Med. Ver., Heidelberg*, 5).—Observations of the constant and regular secretion of the pancreatic juice, by means of a canula in the pancreatic duct of a rabbit, showed that the introduction of mustard or pepper into the stomach caused the secretion to be three or four times as large; the juice was somewhat abnormally watery, but possessed the same digestive properties.

N. H. J. M.

Wandering Cells of the Alimentary Canal. By W. B. HARDY and F. F. WESBROOK (*J. Physiol.*, 1895, **18**, 490—524).—The main bulk of the paper is histological, being a continuation of former work. The cells fall into the three main classes of oxyphile, basophile, and hyaline cells. A noteworthy fact made out is the existence of a layer of basophile cells at the base of the epithelial cells covering the villi. A large number of animals were investigated; in rats fed on a flesh diet, the cells altered to the carnivorous type, the basophile cells becoming more numerous, and scattered and migrated in large numbers between the epithelium cells; the granules of the oxyphile cells

were scarcely preserved by absolute alcohol, and did not stain readily. The absorption of iron appears to be carried out by the hyaline cells.

W. D. H.

The Lactase of the Small Intestine. By FRANZ RÖHMANN and J. LAPPE (*Ber.*, 1895, **28**, 2506—2507; compare Pautz and Vogel, *Abstr.*, 1895, ii, 403).—The authors have investigated the action of the small intestines of calves, oxen, and young and old dogs, on solutions of milk sugar. The intestines were also extracted with chloroform, with thymol solution, and with sodium fluoride solution, and the action of these extracts on the milk sugar studied. In all cases, with the exception of ox intestine, after digestion for several hours, dextrose could be identified in the solution by means of its osazone. Alcohol precipitates from the above extracts of the intestine a substance which will also hydrolyse milk sugar.

Quantitative experiments as to the amount of dextrose formed were also made.

J. J. S.

Influence of the Vaso-motor Nervous System on Metabolism. By F. TANGL (*Pflüger's Archiv*, 1895, **61**, 563—582).—Dogs were curarised, their spinal cord divided in the neck, artificial respiration being kept up. The peripheral end of the spinal cord was stimulated, and observations made on the rectal temperature, and gaseous interchanges before and during stimulation. The general conclusion drawn is that electrical stimulation of the whole vaso-motor system of nerves produces a fall of the temperature of the internal parts of the body, and that this is due not only to increased loss of heat, but also to diminished development of heat.

W. D. H.

Metabolism. By IMMANUEL MUNK (*Pflüger's Archiv*, 1895, **61**, 607—619).—This is a supplementary paper to one previously published (*Abstr.*, 1895, ii, 78), and is chiefly concerned with answering various criticisms, and explaining some parts more fully. The previous general conclusions of the author are maintained.

W. D. H.

Iron in Food. By RALPH STOCKMAN (*J. Physiol.*, 1895, **18**, 484—489).—Almost the only data, with regard to the amount of iron in food, are those of Boussingault (*Compt. rend.*, **74**, 1352), and his results are too high. The great difficulty in work of this kind is complete incineration; which, in the present research, was accomplished by heating the ash with a mixture of hydrochloric and sulphuric acids; the residue was then taken up with dilute sulphuric acid, reduced with zinc, and titrated with potassium permanganate.

The ordinary daily diet was found to contain about 9 or 10 milligrams of iron; but in chlorotic people, who take but little food, the amount was about 3 milligrams. The following articles of diet were also analysed in the same way.

Milk from 2 to 4·3 milligrams per litre.

Oatmeal 3·5 milligrams per 100 grams (dried).

Bread from 0·61 to 0·85 milligrams per 100 grams (dried).

Yellow ox marrow 2·5 to 4 milligrams per 100 grams (dried).

Red calf marrow 7·6 to 8·7

Beefsteak 3·9 milligrams per 100 grams (dried). "

W. D. H.

Sugar as a Food. By B. T. STOKVIS (*Brit. Med. J.*, 1895, ii, 1280—1282). By UGOLINO MOSSO (*ibid.*, 1282). By VAUGHAN HARLEY (*ibid.*, 1282—1284).—These three papers constituted the opening of a discussion at the annual meeting of the Brit. Med. Assoc. (1895). Harley and Mosso support the doctrine that sugar is the great source of muscular energy; this, however, is strongly contested by Stokvis, who severely criticises the ergographic method. W. D. H.

Mannan as Human Food. By C. TSUJI (*Bul. Coll. Agric. Imp. Univ., Tokyo*, 1894, 2, 103—105).—From the tuberous roots of *Concophallus konyaku*, a food, consisting of colourless, gelatinous tablets, is prepared, and is largely consumed in Japan. It is made by mixing the ground root with slaked lime (1 part) and water (2 parts), after which it is boiled with lime water until it forms a gelatinous mass.

When boiled with 3 per cent. sulphuric acid, the root yielded 55·86 per cent. of mannose, assuming the whole of the sugar present to be mannose, as is very probable. The mannan present in the root must be digested by the enzymes in the intestines, and transformed into mannose or a dimannose, corresponding with the maltose made from starch. Attempts to convert the mannan of *konyaku* into a sugar by means of diastase from malt were unsuccessful.

N. H. J. M.

Feeding Experiments on Sheep. By CHARLES D. WOODS and C. S. PHELPS (*Ann. Rep. Storrs Agric. Exp. Stat., Conn.*, 1893, No. 6, 28—42, and 1894, No. 7, 92—106).—In the first series of experiments, five sheep were fed for 12 weeks on a wide ration (maize meal, hay, and turnips), another lot of five being fed with a narrow ration (linseed, pea and maize meal, bran, and hay), after which they were slaughtered, weighed, the various portions separated, and analysed. Similar sheep were slaughtered and analysed at the commencement of the experiments. The second set of experiments was similar, but the sheep were kept in a yard in groups instead of in pens.

The following tables summarise (1) the daily amount of digestible food actually eaten to produce a gain of 1 lb. live weight; (2) the percentage composition of the fresh edible meat produced under the different conditions in both years.

	Organic matter.	Protein.	Fat.	Carbo-hydrates.	Heat value.
	lbs.	lbs.	lbs.	lbs.	cal.
Wide ration, 1893....	6·99	0·82	0·33	5·84	14000
„ 1894....	7·31	0·81	0·38	6·13	14500
Narrow ration, 1893..	6·02	1·23	0·19	4·60	11500
„ 1894..	6·20	1·30	0·25	4·65	12100

	In dry meat.			In fresh meat.			
	Protein.	Fat.	Ash.	Water.	Protein.	Fat.	Ash.
At commencement 1893	41.4	56.1	2.5	58.4	17.3	23.4	1.0
1894	36.6	61.4	2.0	55.2	16.3	27.6	0.9
Wide ration, 1893	34.9	63.2	1.9	57.3	14.9	27.0	0.8
" 1894	32.6	65.6	1.8	52.0	15.6	31.5	0.9
Narrow ration, 1893 ..	36.5	61.5	2.0	58.8	15.0	25.4	0.8
" 1894 ..	35.8	62.2	2.0	54.1	16.1	28.9	0.9

The results show that the character and composition of meat depends largely on the food. The 1893 results illustrate strikingly the fact that water and fat can replace each other to a great extent; whilst the protein is about the same in both series (wide and narrow rations), the meat of the narrow ration animals contains 1.5 per cent. more water and 1.6 per cent. less fat than the flesh of the wide ration sheep. Otherwise the results are not very decisive.

N. H. J. M.

Feeding Experiments with Brushwood. By E. RAMM (*Bied. Centr.*, 1895, **24**, 415—448; from *Landw. Jahrb.*, 1894, **23**, 789—834).—In consequence of the scarcity of food in 1893, experiments were made at Poppelsdorf in which cows, horses, sheep, and goats were partially fed with brushwood. Cows proved to be most suitable for the experiments, as they consumed the material in sufficient quantity, and did not, with one exception, suffer from indigestion. They received a constant ration of sugar beet, dried brewers' grains, earthenut cake and salt, together with wheat chaff (5 kilos.), which was successively replaced by birch (9—12), copper beech (6—11), and hornbeam brushwood (4—5 kilos.) per day. The brushwood was freshly ground each day, and was given in different degrees of fineness.

The effect of brushwood was to decrease the yield of milk, raise the percentage of fat, and, in some cases, to shorten the period of lactation. It was of great importance to have the wood very finely ground. Only the buds and bark seem to have a value as food, a large portion of the wood being found undigested in the faeces. Of the different woods, birch gave the best, hornbeam the worst, results. The following numbers show the percentage composition of fine beech brushwood meal (1), medium and coarse beech (2), copper beech (3), hornbeam (4).

	Dry matter.	Crude protein.	Digestible protein.	Amide nitrogen.	Crude fat.	Crude fibre.	N-free extract.	Pure ash.
1	58.47	3.65	0.70	0.017	3.29	21.24	24.84	0.99
2	62.81	3.35	1.04	—	2.66	27.15	28.54	0.96
3	72.23	3.07	0.68	0.059	1.20	39.77	26.77	1.04
4	81.67	3.43	1.39	0.039	0.94	46.02	30.06	1.14

The percentage amount of lime was (2) 0.389, (3) 0.488, (4) 0.377; of magnesia, (2) 0.107, (3) 0.103, (4) 0.158; of phosphoric acid, (2) 0.143, (3) 0.146, and (4) 0.125.

The results show that in years of scarcity of the ordinary foods, brushwood deserves attention. Some animals, however, cannot be fed with it at all, and it is unsafe to employ it for long periods as an exclusive substitute for forage.

N. H. J. M.

Examination of Foods from Farms where Cattle suffered from Brittleness of the Bones. By OSCAR KELLNER, A. KÖHLER, and F. BARNSTEIN (*Bied. Centr.*, 1895, **24**, 441—443; from *Sächs. landw. Zeit.*, 1894, No. 15).—Analyses were made of five samples of hay and three of straw, produced in the dry season of 1893.

The amount of phosphoric acid was, in every case, very low. There is no direct evidence to show that bone brittleness can arise from want of phosphates, but Förster, Stillnig, and von Mering proved that it may be caused by insufficient supply of lime. Inasmuch as lime and phosphoric acid always occur in the same relative amounts in the bones of young animals, a deficiency of phosphates in the food may cause an insufficient deposit of lime in the bones, and with older animals, deficiency may cause a withdrawal of both phosphoric acid and lime from the bones, which would thus become brittle. The disease can generally be cured by good feeding and a daily allowance of bone meal (30 to 60 grams); on farms where bone softening prevails, the crops should be well manured, especially with soluble phosphates.

Fittbogen showed that plants, when insufficiently watered, are unable to take up phosphoric acid in sufficient amounts.

N. H. J. M.

Action of Drugs on the Embryonic Heart. By JOHN W. PICKERING (*J. Physiol.*, 1895, **18**, 470—483).—This is a series of further experiments in answer to certain criticisms by His (*Centr. Physiol.*, 1894, **8**, 11). The chief points made out are the following:—The combined accelerator and augmentor action of small doses of alcohol on the heart of the embryo chick, reaches its maximum at about 38°; at low temperatures, even small doses of alcohol rapidly depress the cardiac rhythm. A temperature of 40° and upwards has a marked influence on the action of alcohol on the embryonic heart; the frequency becomes too rapid to record, and the force of the beats is much diminished. A dose of alcohol, which, at 20°, is a depressant, has an accelerator action at higher temperatures. The maximum accelerator action of alcohol is attained more rapidly at a lower than at a higher temperature; the depressant action is affected similarly. The cardiac stoppage produced by moderate doses of alcohol at a low temperature can be usually removed by heating, or by the application of electrical stimuli; similarly, the cardiac stoppage produced by small doses of alcohol at a high temperature, can sometimes be removed by cooling; electrical stimulation, however, induces a condition not unlike tetanus. A dose of 0.1 milligram of veratrine (dissolved in 0.65 per cent. sodium chloride solution) acts as a depressant to the embryonic heart at 20°, but, at a temperature above 30°, produces a marked acceleration of cardiac frequency; a dose of 0.3 milli-

gram of veratrine is fatal at 20°, whilst at 42°, the average reduction of cardiac frequency is two beats per minute. Ammonia, acting at 38°, has a marked accelerating action.

Former experiments have shown that in early embryos, before the heart nerves are developed, mascarine has no action; it, however, depresses the cardiac rhythm of chick embryos older than 200 hours, its action culminating in diastolic stoppage, which can be removed by the subsequent application of atropine sulphate, as in frogs. The restoration is only partially complete, if mascarine stoppage has been induced. The action of mascarine nitrate is more marked at sub-normal temperatures, and can often be removed by the application of heat.

W. D. H.

Formation of Blood from Inorganic Iron. By JOS. A. KUNKEL (*Pflüger's Archiv*, 1895, **61**, 595—606).—As a contribution to the disputed question whether inorganic iron is absorbed and contributes to blood (hæmoglobin) formation, experiments were made on two puppies; one received milk, in which the amount of iron was ascertained, the other the same food *plus* iron. The milk contained about 1 milligram of metallic iron (1·4 milligram Fe_2O_3) per litre. The extra iron given daily was 30 drops of liquor ferri albuminat of the German Pharmacopœia (= 4·4 milligrams of iron). During life, the blood was examined at weekly intervals. After death, other organs were submitted to analysis. The main facts are given in the following table. It shows a greater amount of iron in the dog to which iron had been administered.

Percentage of Fe_2O_3 in blood in successive weeks	Dog A, with iron.		Dog B, without iron.	
	1. 0·0486 2. 0·0388 3. 0·0286 4. 0·0334	5. 0·0363 6. 0·0384 7. 0·0348 —	1. 0·0443 2. 0·0503 3. 0·0259 4. 0·0303	5. 0·0234 6. 0·0227 7. 0·0195 —

After death.	Weight.	Total Fe_2O_3 .	Weight.	Total Fe_2O_3 .
	grams	gram	grams	gram
1. Total blood	—	0·0404	—	0·0252
2. Liver	133·8	0·0317	151·2	0·0043
3. Spleen	7·2	0·0043	7·3	0·0013
4. Kidneys	27·0	0·0025	30·2	0·0014
5. Ribs	11·1	0·0011	9·9	0·0001

Physiology of Blood Sugar. By F. TANGL and VAUGHAN HARLEY (*Pflüger's Archiv*, 1895, **61**, 551—559).—Most physiologists look on the liver as the source of the sugar in the blood; support is lent to this doctrine by the fact that if the liver is excised or excluded from the circulation, sugar disappears from the blood. Interference with the circulation of the liver by ligature of the intestinal arteries lessens its activity (compare Slosse, *Du Bois Reymond's Arch.*, 1890, 482, on

the diminution in urea so produced), and the present experiments in dogs show that this is true for its sugar forming function; the quantity of sugar in the blood markedly diminishing (from 42 to 92 per cent. in different experiments) after the ligature of the arteries in question.

W. D. H.

Circulation Time. By GEORGE N. STEWART (*Brit. Med. J.*, 1895, ii, 1287).—The method employed consists in the injection of methylene blue into a vein and watching for its appearance in the carotid artery. It is not necessary to open the artery. This simple method gives identical results with the electrical method of the author. The mean pulmonary time in a dog is 9.55 seconds; and in different animals this varies as the diameter of a sphere of the same mass as the animal, and having the same specific gravity. The circulation time in a man is probably about 15 seconds, which is considerably shorter than that stated by the older experimenters.

W. D. H.

Muscular Work and Glycogen. By FR. SCHENCK (*Pflüger's Archiv*, 1895, 61, 535—543).—Seegen (*Du Bois Reymond's Archiv*, 1895, 242), from experiments on dogs in which he stimulated the nerve of the quadriceps muscle, concludes that the glycogen which disappears will account for only five per cent. of the work done. He looks on the sugar of the blood as the normal source of muscular energy, and glycogen as a reserve called into use only when work is excessive.

The present article traverses these statements, and speaks in favour of Pflüger's theory. The chief objections raised are that the work done in Seegen's experiments was not maximal, and that no proof is given that the glycogen which disappears is burnt up; it might, as indeed Seegen appears to admit, be converted into sugar, how then is the sugar of the blood to be distinguished from that originating from glycogen?

W. D. H.

Proteïds of Muscle Plasma. By OTTO VON FÜRTH (*Arch. exp. Path. Pharm.*, 1895, 36, 231—274).—Muscle plasma was obtained from muscles free from blood by extracting them with physiological salt solution. This coagulated spontaneously, and the clotted proteïd formed is called myogen-fibrin, or myosin-fibrin. The proteïds in the muscle plasma are three in number, namely paramyosinogen 17 to 22 per cent. of the total proteïd, myosinogen or myogen 77 to 83 per cent. of the total proteïd, and traces of serum albumin probably derived from the remains of blood and lymph left in the muscles. The whole paper is written very largely in reference to previous work by Kühne and Halliburton (*Abstr.*, 1887, 984).

The work of Halliburton is confirmed in its main point, namely that there are two proteïds in the muscle plasma, paramyosinogen and myosinogen which enter into the formation of the muscle clot; the action of a specific ferment to bring about this change was not specially investigated. The principal new fact made out is that paramyosinogen passes into this condition of myosin-fibrin directly; whilst in the passage of myosinogen into the state of myogen-fibrin,

there is an intermediate soluble stage coagulated by heat at the remarkably low temperature of 40°.

Paramyosinogen is a typical globulin, and is regarded as identical with Kühne's myosin. *Myosinogen* is described as differing from a globulin in many particulars; it is spoken of as a proteid *sui generis*.

The proteid in the muscle serum, described as myoglobulin by Halliburton, is not regarded as a definite substance, but only as a part of the myosinogen which has escaped coagulation. The phenomenon described by Halliburton as re-coagulation of myosin, is regarded only as a reprecipitation of globulin.

Peptones, albumoses, nucleo-proteids were not found (compare Whitfield, Abstr., 1894, ii, 358).

The muscle plasma from fishes' muscle contains another proteid called *myoproteid*. It gives the usual proteid reactions, and is readily digested by gastric juice; it is neither coagulated by heat, nor precipitable by removing the salts by dialysis. It is precipitated by neutral salts like globulins. It is precipitable by acetic acid, but is neither a mucin nor a nucleo-proteid. The same substance was found in crab's muscle.

W. D. H.

Antagonism between Salts of Calcium and those of Sodium, Potassium, and Ammonium. By SYDNEY RINGER (*J. Physiol.*, 1895, 18, 425—429).—Milk to which rennet and calcium chloride have been added clots readily, whilst the presence of sodium chloride hinders, or in larger amounts prevents, this action; the chlorides of potassium and ammonium act similarly, but less powerfully than that of sodium. This antagonism is limited to the precipitation of the casein as a clot, and does not affect the chemical change from caseinogen to casein produced by the rennet ferment. The same antagonism exists in relation to blood clotting, and to muscular contraction as evidenced by experiments on the frog's heart, only in the last case potassium chloride is a more powerful antagonist than sodium chloride.

W. D. H.

Toxic Substance from the Supra-renal Capsules. By D. GOURFEIN (*Compt. rend.*, 1895, 121, 311—314).—The glycerol extract of the supra-renal capsules contains proteids which are precipitated by alcohol, and have little or no toxic effect, together with substances which are not precipitated by alcohol and are highly toxic. As the latter are not decomposed by heat, the capsules can be extracted with hot water, the solution precipitated by alcohol, and the clear liquid evaporated on a water bath. The product when injected subcutaneously causes death in a short time, and seems to act on the central nervous system. The proportion of the poison in the supra-renal capsules is variable, but no similar effects are produced by extracts of the spleen or the muscle of the same animals treated in the same way.

C. H. B.

Succus Entericus of Sheep. By FRITZ PREGL (*Pflüger's Archiv*, 1895, 61, 359—406).—The intestinal juice has been investigated chiefly in carnivora. The only previous experiments on herbivora were made on a goat by Lehmann, who found the juice had no digestive action. The present experiments were made on a lamb.

The juice was collected by a modification of the Thiry-Vella method, from 3 to 5 grams of juice being obtained from the loop per hour. It is a mucous, strongly alkaline fluid, which is rich in proteid, and tends, like pancreatic juice, to set into a jelly spontaneously; its specific gravity is about 1.014. It contains about 0.2 per cent. of urea. The following analysis is given in parts per 1000.

Sodium carbonate	3.69
Albumin and globulin	18.09
Albumoses and mucin	1.27
Urea	2.29
Other organic substances	3.31
Ash	1.27
Water	970.05

On proteids, cellulose, pentoses, and fats, it has no digestive action, but it converts starch and glycogen into dextrose with intermediate dextrins; it inverts cane sugar and maltose, but not lactose.

W. D. H.

Artificial Hydræmic Plethora. By J. B. LEATHES (*Brit. Med. J.*, 1895, ii, 1287).—The experiments briefly recorded go against the secretion theory of lymph formation.

W. D. H.

Physical Factors in Absorption. By HARTOG J. HAMBURGER (*Brit. Med. J.*, 1895, ii, 1287).—The disappearance of fluids from the serous cavities can take place either by the lymphatic or blood vessels; the process is not one of osmosis, for both isotonic and hypertonic solutions disappear, and Heidenhaim concluded that a vital activity of the epithelium must occur to account for the phenomena. Absorption occurs, however, in a dead animal. The force at work is believed to be imbibition of the molecular kind, such as occurs with gelatin and other homogeneous substances, and this imbibition may be exhibited by the cells or by the cement substance between them; this is of course limited in a dead animal, but in a living one the circulating fluid removes the absorbed liquid.

A working model to illustrate this has been constructed as follows: a cylinder of gelatin is taken to represent a capillary, and enclosed within a wider glass cylinder to represent the tissue spaces; both cylinders are now filled with a fluid like serum, and if a stream is kept up through the gelatin cylinder, the fluid is absorbed from the space between the two cylinders, and is replaced by fresh fluid allowed to flow in through a side tube. The hydrostatic pressure of the fluid is also to be taken into account.

W. D. H.

Potassium Thiocyanate in Saliva. By IMMANUEL MUNK (*Pflüger's Archiv*, 1895, 61, 620—622).—In reference to Nencki's work on thiocyanic acid in the stomach, it is pointed out that in the dog, it is absent in the saliva; horse's saliva is also free from it.

W. D. H.

Elimination of Calcium Compounds in Rachitis. By WILLIAM OECHSNER DE CONINCK (*Compt. rend.*, 1895, 121, 262—263).—

In cases of rachitis, the quantity of calcium in the urine gradually diminishes in the same manner as the quantity of magnesium. When elimination of magnesium is small, however, that of calcium is relatively high, and this result has led the author to conclude that in rachitis the calcium of the osseous system is partially replaced by magnesium. Chabrié has arrived at a similar conclusion with respect to osteomalagia (compare Abstr., 1895, ii, 455).

C. H. B.

Urobilin. By ADOLF JOLLES (*Pflüger's Archiv*, 1895, 61, 623—637).—Urobilin was first described by Jaffé in febrile urine, later, Maly obtained from bilirubin, by reduction, a substance he called hydrobilirubin, which he considered to be identical with urobilin, and Vierordt pointed out that normal urine contains other pigments as well. MacMunn distinguishes between normal urobilin and febrile or pathological urobilin, which differ in their optical characters; fresh urine containing little or no urobilin often becomes darker on exposure to the air, and this he considers to be due to the oxidation of a chromogen, urobilinogen. Both MacMunn and Hoppe-Seyler have obtained urobilin by artificial means from hæmatin. MacMunn and Le Nobel both doubt the absolute identity of urobilin and hydrobilirubin. Pathological urines, dark from the presence of supposed bile-pigment, have shown in many cases, on examination, that the increase of urobilin is the cause of the deep colour of the urine (urobilin-icterus); whilst recently A. Katz (*Wiener Med. Woch.*, 1891, Nos. 28—32) has shown that this increased excretion of urobilin is due to metabolic changes having their seat in the liver, which if they are prolonged produce harmful changes in the liver cells.

The present paper points out that urines containing a small amount of bile-pigment will, after standing exposed to the air for several days, no longer show any bilirubin whatever, urobilin having taken its place. The source of the urobilin in the fæces is also doubtless the bile-pigment, unaltered bile-pigment never occurring in normal fæces. Urinary urobilin shows two well-marked characters: (1) a green fluorescence, which appears when the urine is rendered alkaline with ammonia and a few drops of zinc chloride solution are added; (2) a well-defined absorption band between the lines *b* and *F*; it was necessary to determine if any other urinary pigments give the same characters. Gmelin's test for bile-pigment consists in adding fuming nitric acid; the colour changes to blue, violet, red, brown, and finally yellow, the yellow end product of oxidation being called choletelin; these coloured products, with the exception of the last, when reduced by zinc and hydrochloric acid, all show absorption bands, and give with ammonia and zinc chloride a green fluorescence. The absorption bands given by the red and brown pigments are in the neighbourhood of the *F* line, but not so sharply defined as in the urobilin spectrum, which, however, they closely resemble. In some urines, pigments can be separated which give all the characters of the red and brown oxidation products of bilirubin, whilst others again yield a substance identical with choletelin, which is the highest oxidation product of bilirubin, and is, in fact, regarded as the yellow pigment of normal urine; for the details of the method of separating the pigment

from urine by lead acetate, &c., the original paper must be consulted. In conclusion, two classes of urobilins are distinguished from one another, *pathological urobilins*, which are reduction products of bilirubin, and *physiological urobilins*, which are oxidation products of bilirubin. These terms are used in a different sense from that in which MacMunn uses the terms normal and pathological urobilin; but the idea that normal or physiological urobilin is an oxidation product of blood or bile-pigment should be credited to MacMunn. Among the physiological urobilins is reckoned the substance which darkens on exposure to the oxygen of the air.

The source of physiological urobilin is considered to be the bile-pigment; pathological urobilin has usually the same origin, but it can come from blood pigment directly after extravasations of blood.

W. D. H.

Action of Anæsthetics on Nerve. By AUGUSTUS D. WALLER (*Proc. Physiol. Soc.*, 1895, 45—47).—A frog's sciatic nerve is laid on two pairs of electrodes, one pair being exciting, the other pair non-polarisable, and leading to a galvanometer; on excitation, the electrical change in the piece of nerve connected with the electrodes is noticed. The whole is contained in a chamber, through which gases or vapours in known amount can be passed. In large amount, carbonic anhydride produces primarily abolition, secondarily augmentation of the effect observed, whilst in small amount (for instance, with expired air) there is primarily augmentation. Ether produces prolonged abolition, followed in time by recovery, whilst chloroform produces abolition, but no recovery occurs; other anæsthetics were also investigated.

The most important point made out is regarded as evidence of the production of carbonic anhydride in the nerve itself, consequent on activity, for after prolonged excitation the effects of intermittent stimulation is to produce an increase of the galvanometric change, just as though a small percentage of the gas had been added to the surrounding air.

W. D. H.

Action of Carbonic Oxide on Man. By JOHN S. HALDANE (*J. Physiol.*, 1895, 18, 430—462).—The experiments made by the author on himself show that the symptoms caused by carbonic oxide depend on the extent to which the hæmoglobin has been saturated; the percentage saturation of the hæmoglobin of the red corpuscles may be estimated during life by a simple colorimetric method. Carbonic oxide is a "cumulative" poison. The symptoms do not become sensible during rest until the corpuscles are about one-third saturated; with half saturation, the symptoms (respiratory distress, headache, &c.) become urgent. Similar symptoms are experienced by mountaineers at high altitudes.

When air containing this gas is breathed, about half of that actually inhaled is absorbed, except when absorption is coming to a standstill. The time required for the production of sensible symptoms in an adult depends on the time required for the inhalation of about 660 c.c., or the absorption of about 330 c.c. of the pure gas; this time in different animals varies with the respiratory exchange per

unit of body weight, and is about 20 times as long in a man as in a mouse; hence a mouse can be used as an indicator in a coal mine before men penetrate into it.

The maximum amount of carbonic oxide capable of being absorbed by the blood from air containing a given small percentage depends on the relative affinities of oxygen and carbonic oxide for hæmoglobin, and the relative tension of the two gases in arterial blood. The affinity of carbonic oxide for hæmoglobin is about 140 times that of oxygen, and the oxygen tension of human arterial blood is, approximately, 16 per cent. of an atmosphere. Distinct symptoms, appreciable during rest, are not produced until about 0.05 per cent. of the gas is present; with about 0.2 per cent. urgent symptoms are produced. With a given percentage of carbonic oxide in air, a certain percentage saturation of the blood is reached within about 150 minutes, and is not afterwards exceeded, however long the breathing of the vitiated air is continued. The disappearance of the gas from the blood when fresh air is again breathed is always much slower than the absorption of the gas, and is chiefly due to dissociation of carbonylhæmoglobin by the mass influence of the oxygen in the pulmonary capillaries, and consequent diffusion of the gas outwards through the alveolar epithelium.

W. D. H.

Chemistry of Vegetable Physiology and Agriculture.

Fermentation by Apiculated Yeast: Influence of Aëration on Fermentation by Elliptical Yeast at a High Temperature. By M. RIETSCH and M. HEISELIN (*Compt. rend.*, 1891, 121, 378—380).—When musts prepared from dry grapes, with or without the addition of saccharose, are fermented under similar conditions, the ratio of alcohol produced to sugar destroyed is higher with elliptical yeast than with apiculated yeast.

Moderately dilute musts, fermenting with elliptical yeast at about 36°, are not appreciably affected by passing a current of air through them, but with stronger musts, the aëration produces a distinct increase in the amount of alcohol, and the beneficial effect is greater the stronger the must. In all cases, however, the advantage gained by cooling the liquid to about 30° is much greater than that resulting from aëration, although the latter is still beneficial. A combination of the two processes gives the best results, and is especially to be recommended in hot countries, in which the musts are usually somewhat concentrated. Precautions must of course be taken against acetic fermentation.

C. H. B.

Effect of abundant Application of Nitrogen on the Assimilation and Respiration of Plants. By H. MÜLLER (*Bied. Centr.*, 1895, 24, 454—456; from *Jahresber. deut.-schweiz. Versuchs-stat., Wädenswil*, 3, 52).—The results of the experiments which were made with potatoes and sugar beet were as follows. The application

of large amounts of nitrogen to the plants caused increased leaf-development with greater percentage of chlorophyll; starch formation in the leaves was impeded, the starch was more quickly dissolved, and there was less storage of reserve substances; the amount of glucose was increased, and there was increased decomposition of nitrogen compounds, resulting in increased respiration of all parts, and in increased growth.

With both plants, excessive or exclusive nitrogenous manure should be avoided. Roots which have been too heavily manured with nitrogen should be used first, as they are the most subject to loss through respiration.

N. H. J. M.

Consumption of Asparagine in the Nutrition of Plants.

By Y. KINOSHITA (*Bull. Coll. Agric., Imp. Univ., Tokyo*, 1895, 2, 196—199).—According to C. O. Müller (*Abstr.*, 1887, 70), regeneration of proteids from asparagine can only take place in green leaves, light and the nascent state of carbohydrates being essential. In order to ascertain whether the process would go on in the dark, shoots of soja bean, which are rich in asparagine, were fed with organic solutions, and examined from time to time for asparagine. The solutions selected were: (1) 1 per cent. methylic alcohol with one-tenth of its bulk of saturated gypsum solution; (2) 1 per cent. glycerol solution with gypsum, and (3) glucose solution. When placed in these solutions, the plants were 20—27 cm. long, and the roots and stems were rich in asparagine; the cotyledons had been removed. Tests for reserve albumin, made during the experiment, showed it to be absent in the control experiment, and present in considerable amount in the shoots grown in sugar and glycerol. After about four weeks, the shoots of the control experiments showed a higher percentage of asparagine in the dry matter (28·7) than at the commencement (21·5 per cent.), whilst the shoots in methylic alcohol and glycerol solutions showed a respective reduction to 18·9 and 13·7 per cent. The production of dissolved proteids was thus coincident with decrease of asparagine. The increase in amount of asparagine in the control experiments was probably due to production from other amides. A less increase was observed in another control experiment (24·0) in which the cotyledons had not been removed, probably due to the protecting effect of the galactans and other carbohydrates gradually becoming soluble.

Glycerol and methylic alcohol supplied to the roots can, therefore, not only hinder the production of asparagine in the shoots, but also diminish the amount already present. Glycerol is the more effective; it also forms sugar. Since the shoots grew better in these solutions than in water, and showed the presence of dissolved proteids, it may be assumed that both methylic alcohol and glycerol can regenerate proteids from asparagine. Moreover, light cannot have any direct action in supporting the process, although it is indirectly of great importance in yielding the necessary carbohydrates.

N. H. J. M.

Assimilation of Nitrogen from Nitrates and Ammonium Salts by Phaenogams. By Y. KINOSHITA (*Bull. Coll. Agric., Imp. Univ., Tokyo*, 1895, 200—202).—Barley was sown in sand con-

tained in three pots, and kept dark. After 16 days, the plants of one pot were taken out and analysed, whilst those of the second and third pots were watered with a 1 per cent. solution of ammonium chloride and a solution containing an equivalent amount of sodium nitrate respectively; 500 c.c. of each solution was used during the week the experiment lasted. In a second experiment, maize plants, nearly 40 cm. long, were placed in solutions of ammonium and sodium nitrates (containing 1 per cent. of nitrogen), control plants being placed in distilled water. The following total amounts (in grams) of nitrogen, and of nitrogen as asparagine, were found.

	At commencement.		At conclusion.	
	Total.	As Asparagine.	Total.	As Asparagine.
Barley in AmCl .. } NaNO ₃ .. }	3·512	0·656	{ 4·436 4·923	2·027 0·977
Maize in AmNO ₃ .. } ,, NaNO ₃ .. }	4·13	0·38	{ 4·23 4·15	0·73 0·24

The results of these preliminary experiments make it evident that ammonium salts are transformed into asparagine, whilst nitrates are not, and it seems certain that asparagine is the form in which the excess of nitrogen, originally in ammonium salts, is stored up.

N. H. J. M.

Reserve Protein in Plants. By G. DAIKUHARA (*Bull. Coll. Agric., Imp. Univ., Tokyo*, 1895, 2, 189—195; compare Abstr., 1895, ii, 128).—The plants previously examined (*loc. cit.*) for active albumin were collected in the spring. It seemed possible that, owing to transportation, leaves found rich in active albumin in the spring might no longer contain it in the autumn, or that, on the other hand, plants of rapid growth which gave a negative reaction in the spring might accumulate active albumin in the autumn. An examination of a number of plants collected in the autumn gave, however, generally, results similar to those previously obtained, except that plants which gave a positive result in the spring usually showed less active albumin in the autumn.

Repeated examination of partly dead leaves showed that they always produced proteosomes with caffeine in the healthy cells, even when very close to the dead portions, but the dead portions invariably gave negative results.

The frequent occurrence of active albumin in the flower may be of importance to seed formation; so far, active albumin has generally been found only in the epidermis of the seeds and fruits examined.

N. H. J. M.

Formation of Proteids in Plant Cells. By OSCAR LOEW (*Bull. Coll. Agric., Imp. Univ., Tokyo*, 1894, 2, 43—67).—*Micro-organisms and Mould-Fungi*.—The behaviour of aerobic microbes and moulds towards different organic compounds indicates that the proteids and proto-

plasma remain in one species the same, and that the formation of proteïds commences with relatively simple atomic groups.

As regards carbon compounds, the nutritive quality of acids is increased by the entrance of alcoholic hydroxyl, that of alcohols increases with the number of HO-groups; aldehyde and ketone groups increase the nutritiveness, the lower members of the fatty acids being more assimilable than the higher. Unsaturated ring systems are generally unfavourable, whilst some compounds (such as quinic acid) containing a saturated benzene ring are very nutritive. Pyridine, pinacone, ethylenediamine, amidoacetal, glyoxal, meconic and oxalic acids do not support bacterial growth; acetoxime, diacetoneamine, citraconic and maleïc acids do, but only with difficulty; at the same time, none of these compounds is so poisonous as to kill the bacteria, if well nourished. It is of interest that whilst with maleïc acid it takes weeks to develop bacteria, fumaric acid supports bacteria well; in citraconic acid there was no development for six weeks. Comparing the different monhydric alcohols, it was found that whilst 1 per cent. methylic alcohol readily develops bacterial growth, amylic alcohol has to be used diluted to 0.1 per cent. The fatty acids decrease in nutritive properties as their molecular weight increases; formic acid, however, seems to be available only in the case of one kind of bacterium (*Centr. f. Bacteriol.*, 12, No. 14); formaldehyde is poisonous, but its combinations with hydrogen sodium sulphite, and with ammonia can be utilised by a bacillus and by a kind of *Dematium*.

As regards the manner in which acetic acid, for instance, is utilised, it is supposed that it is oxidised with formation of formaldehyde, carbonic anhydride, and water; this would explain the favourable effect of the $\text{CH}\cdot\text{OH}$ -groups or the isomeric formaldehyde. In the case of the utilisation of formic acid (sodium salt), there would probably be first a transformation into glyoxylic acid, and then decomposition of this into formaldehyde and carbonic anhydride. Oxalic and parabanic acids and urea, &c., cannot be used as sources of carbon, because they cannot furnish formaldehyde. There is at present no explanation for the difference in the value of the stereoisomeric, maleïc, and fumaric acids. As a rule, compounds containing the groups CH_3 , CH_2 , $\text{CH}\cdot\text{OH}$, and $\text{CH}_2\cdot\text{OH}$ can be used as sources of carbon, if not poisonous, and if not too resistant to the attacks of bacteria. In the following lists (next page) the various compounds are grouped thus: I, very good sources of carbon; II, moderately good; III, very poor; and IV, useless, so far as observed:—

The very remarkable observation of Hüppe (*Biol. Centr.*, 7, 702), that the nitrifying bacteria will develop in inorganic solutions may be explained by assuming part of the hydrogen of the ammonia to act on carbonic anhydride to form formaldehyde and water, and the subsequent condensation of the formaldehyde to sugar.

Substances which support the life of aerobic bacteria are generally, but not always, suitable for mould-fungi. Compounds differ considerably in their power of developing fungi, for whilst isobutylic alcohol yields 9–10 per cent. of fungoid matter, asparagine yields nearly 22 per cent. Maleïc, citraconic, mesacouic, dibenzylmalonic, and diethylsuccinic acids cannot be utilised by moulds, whilst

malonic, succinic, and methyl- and ethyl-succinic acids are well utilised. With regard to nitrogen, potassium ferrocyanide is not a very suitable compound, whilst hydroxylamine and diamide are poisons; azoimide can only be used highly diluted. The nitrogen compounds have always to be transformed into ammonia before protein formation can begin; anaërobic microbes effect this by reduction, aërobic by oxidation. In the assimilation of elementary nitrogen by microbes, ammonium nitrite is probably first formed, and the nitrous acid rapidly reduced to ammonia.

I.	II.	III.	IV.
Glycerol. Mannitol. Sugars. Lactic acid. Succinic acid. Tartaric acid. Citric acid. Betaïne.	Methylic alcohol. Ethylenic glycol. Acetone. Acetic acid. Fumaric acid. Pyruvic acid. Levulinic acid. Glycocine.	Phenol. Acetoxime. Diacetoneamine. Valeric acid. Maleic acid. Citraconic acid. Benzoic acid. Lecithin.	Pinacone. Sulphonal. Amidoacetal. Oxalic acid. Meconic acid. Picric acid. Antipyrine. Dimethyloxy- <i>m</i> - diazine.
Alanine. Leucine. Asparagine. Glutamine. Creatine.	Methylamine. Choline. Allantoin. Caffeïne. Methylic cyanide.	Trimethylamine. Strychnine. Hexamethyleneamine. Amidobenzoic acid. Glyoxylic acid.	Ethylenediamine. Pyridine. Urea. Parabanic acid. Guanidine.

Sulphur seems to be present in the proteïds of fungi, as in other proteïds, as $\cdot\text{SH}$. Sulphates have, therefore, to be reduced. Sulphonal, $\text{CMe}_2\cdot\text{SO}_2\text{Et}_2$, is a suitable source of sulphur in presence of easily assimilable carbon, but not otherwise.

Chlorophyll Plants.—In the higher, as in the lower plants, it must be assumed, whatever compounds are utilised for their growth, that the carbon compounds are so broken up as to produce formaldehyde, and that the nitrogen must be liberated as ammonia. As regards the different forms of nitrogen produced by the decomposition of proteïds, asparagine, leucine, and tyrosine, phenylamidopropionic and amidovaleric acids, arginine and allantoin have been found; urea has not been detected, but guanidine occurs in the shoots of *Vicia sativa*. Schulze's observation that whilst amido-acids formed during the first period of germination decrease in quantity, asparagine increases, is of very great importance; when sugar takes part in the formation of proteïds from asparagine, it furnishes the deficiency of carbon. Proteïds might be formed in the following manner:—By reduction in presence of glucose, asparagine might yield aspartic aldehyde, and the ammonia liberated would immediately, in presence of glucose, form another molecule of aspartic aldehyde; 3 mols. of this aldehyde ($\text{C}_4\text{H}_7\text{NO}_2$) may be supposed to condense with elimination of water (2 mols.), and yield an intermediate compound, ($\text{C}_{12}\text{H}_{17}\text{N}_3\text{O}_4$), 6 mols. of which, with hydrogen (6 mols.) and hydrogen sulphide (1 mol.), would yield albumin of the formula $\text{C}_{72}\text{H}_{112}\text{N}_{18}\text{SO}_{22}$, and water (2 mols.). Glucose would again be required for the reduc-

tion. On the assumption that the aldehyde and amido-groups are prevented from acting on each other, and that in the reduction the 12 aldehyde groups are converted into secondary alcoholic groups, $\text{CH}\cdot\text{OH}$, the final product (active albumin) would be of extraordinary lability, containing 12 aldehyde and 18 amido-groups in 1 mol. With the loss of its aldehyde character it would be changed to passive albumin. It is obvious that passive albumin is not produced by direct synthesis, but is the product of the transformation of the directly formed active, unstable albumin. N. H. J. M.

Active Albumin as Reserve Material in Plants. By OSCAR LOEW (*Bull. Coll. Agri., Imp. Univ., Tokyo*, 1894, 2, 23—33).—The author and Bokorny have shown the presence in plants of a protein substance, apparently in solution, which gives certain reactions, of which living protoplasm, owing to its great lability, is incapable, and which neither dead protoplasm nor the known soluble proteids show. The substance has the rôle of a reserve material, being used up during the growth and multiplication of cells.

Many algæ and parts of higher plants show, under the influence of caffeine (0.1—0.5 per cent.) or of antipyrine (0.5 per cent.), a number of minute, transparent, colourless globules, which gradually unite to form larger globules or droplets, at the same time losing their original motions; all the *Spirogyræ* are specially adapted for these observations. When the objects are placed in water, the globules disappear, as the caffeine leaves the cells by osmosis, and the cells continue to live as before the treatment; if, however, the cells die during the treatment, or are killed by poisons, the droplets also change their properties, thus showing close chemical resemblance of the matter in the protoplasm and in the droplets, the latter becoming turbid, and losing their solubility. When spirogyra-threads, containing freshly formed droplets, are exposed to ether vapour, the cells are killed in a few seconds, and, in about 20 minutes, the globules lose their brightness and their solubility.

In the dissolved state, the substance is quickly changed by the death of the cells in which caffeine never produces globules. *Spirogyra Weberi*, treated for one minute with very dilute aqueous iodine, yields globules with caffeine, but not after 10 minutes' treatment with iodine.

The substance is, therefore, a proteid differing from ordinary soluble proteids by being separated in globules by caffeine, &c., and by its very great lability. In the coagulated state, the globules show all the properties of ordinary coagulated proteids. When the proteosomes, as these globules are termed, are treated with ammonia they are solidified, the ammonia entering into intimate combination. This fixation of ammonia, which recalls the formation of pyrrolines from 1 : 4 ketones, is explained by the presence of aldehyde groups in the proteosomes, which are able to reduce silver nitrate, even after treatment with ammonia; the reaction with silver nitrate was also obtained with the proteosomes of *Symphoricarpus racemosus*, which is free from tannin, and from which every trace of sugar was removed.

The fact that proteosomes represent the active albumin was proved by cultivating *Spirogyra* in nutritive solutions without and with nitrogen (potassium nitrate). In the first case, the stored-up albumin was used up so thoroughly that, after two or three weeks, caffeine failed to produce proteosomes; whilst in the second case, there was an intense formation of proteosomes with caffeine after three weeks, more active albumin having been produced than was required. Changes of temperature have great influence on the amount of active albumin present, and phosphates interfere with its accumulation (Loew, "Physiol. Functions of Phosphoric acid," *Biol. Centr.*, 2, 280).

Active albumin was found in a great variety of plants and in various parts of plants, but not in animals.

The separation of globules by caffeine or antipyrine is probably due to a very loose combination in which the original chemical nature of the albumin is not otherwise altered, but it is also possible that the bases effect a loose kind of polymerisation; at any rate the original state may be restored by washing out the bases with water. Stronger bases (guanidine, methylamine, &c.) produce granules which do not form droplets, and which soon became insoluble in water; inorganic bases produce minute granules and rapid death of the cells (compare Loew and Bokorny, *D. chem. Kraftquelle im lebenden Protoplasma*, München, 1889; *Bot. Centr.*, 1889 and 1893; *Flora*, 1892, 127; Bokorny, *Prings. Jahrb.*, 19 and 20; *Pflüger's Archiv*, 45 and 50).

N. H. J. M.

Function of Diastase in Plants. By J. Grüss (*J. Pharm.*, 1895, [6], 2, 275—276; from *Apoth. Zeit.*, 1895, 307).—Diastase may be readily detected in the cells of plants by digesting the tissue, for a sufficient length of time, with a solution of guaiacum in absolute alcohol, and then immersing sections of it in a dilute solution of hydrogen peroxide; a fine blue colour is developed in those cells which contain the enzyme.

The author finds that diastase is always present in those parts of the plant from which it is necessary that starch should be removed for purposes of nutrition.

As the amylolytic power of diastase is inhibited by the presence of more than a certain limiting amount of glucose, it would seem that in assimilation, the formation of glucose precedes that of starch, and continues as long as the sugar is removed by circulation. When, however, the sugar commences to accumulate beyond the requirements of the organism, it undergoes polymerisation to maltose and eventually to starch, which, in the presence of glucose, is not hydrolysed by the diastase; as soon, however, as the glucose is reduced by circulation below the inhibitory proportion, the starch is hydrolysed by the diastase, and the supply of soluble nutritive material thus maintained.

The amylolytic power of diastase is increased in presence of salts of the alkalis and alkaline earths, and by asparagine, &c.

JN. W.

Hydrogen Peroxide in Plants. By J. CHO (*Bull. Coll. of Agric., Imp. Univ., Tokyo*, 1895, 2, 225—227).—A reply to Bach (Abstr., 1895, ii, 239). Twenty-one species of plants were treated as described by Bach. In nine cases, a coloration was observed, but not the colour produced in the control experiment; moreover, the extracts gave the same reaction after treatment with platinum black, which would have destroyed any hydrogen peroxide, if it had been present. The coloration observed is probably only obtained when the leaves have been partly killed by the oxalic acid solution, so that certain readily oxidisable compounds are enabled to leave the cells by osmosis, and yield coloured products by oxidation in presence of aniline oxalate.

N. H. J. M.

Occurrence of two kinds of Mannan in the Roots of *Conophallus Konyaku*. By Y. KINOSHITA (*Bull. Coll. Agric., Imp. Univ., Tokyo*, 1895, 2, 205—206).—It was shown by Tsuji (this vol., ii, 44) that the root of *Conophallus* contains a large amount of an anhydride of mannose; it is now shown that two kinds of mannan are present. The finely ground root was repeatedly extracted with boiling water until the extract was no longer slimy. The residue yielded mannose when boiled with dilute acid, and the slimy extract, on the addition of alcohol, yielded a copious, nearly white, flocculent precipitate; the latter, when dried at 100°, was no longer soluble in water, but yielded mannose when boiled for some hours with 4 per cent. sulphuric acid. This mannan differs from that obtained from yeast by Salkowski (Abstr., 1894, i, 222) in losing its solubility on drying, but agrees in its behaviour with basic lead acetate (no precipitate), ferric chloride, and ammonia (gelatinous precipitate), copper sulphate and sodium hydroxide (thick, blue precipitate), and also with Fehling's solution.

The slimy mannan was not altered by the diastase of malt, by invertase, or emulsin, and Osawa's experiments on dogs showed that it is digested with much more difficulty than starch. An enzyme capable of saccharifying the mannan must, however, exist in the *konyaku* root, and the author hopes to isolate it.

N. H. J. M.

Composition of some Mucilages. By K. YOSHIMURA (*Bull. Coll. Agric., Imp. Univ., Tokyo*, 1895, 2, 207—208).—The slimy extracts of the various plants were concentrated, precipitated with alcohol, the washed precipitates boiled with sulphuric acid (2—4 per cent.), neutralised with barium chloride, filtered, and concentrated to syrups. Portions of these were evaporated with nitric acid and examined for mucic acid, other portions were mixed with phenylhydrazine acetate, whilst others again were examined with phloroglucinol and hydrochloric acid for pentoses. Finally, the osazones were prepared.

The mucilage of *Sterculia plantanifolia* (young shoots) consists of araban with some galactan; that of *Colocasia antiquorum* (tuberous roots) probably consists only of a polyanhydride of diglucose. The mucilages of *Vitis pentaphylla* (stems and leaves), and *Opuntia* (fleshy stems), chiefly consist of galactan, those of *Oenothera Jaquinii* (stems and leaves), and *Kadzura japonica* (young leaves and stems), contain galactan and araban.

N. H. J. M.

Laccase in Vegetables. By GABRIEL BERTRAND (*Compt. rend.*, 1895, 121, 166—168).—An alcoholic solution of gum guaiacum becomes blue in presence of air and a very small quantity of laccase; if the proportion of the latter is considerable, the blue coloration may change to green and eventually to yellow. This reaction is very convenient as a test for laccase, and by means of it, combined in most cases with the actual isolation of the laccase, the author has recognised the presence of this substance in the roots of the beet, carrot, and turnip, the tubers of the dahlia, potato, and Jerusalem artichoke, the rhizome of balisier, apples, pears, chestnuts, quinces, lucern, clover, rye-grass, asparagus, and the flowers of the gardenia. As a rule, only those organs of the plant which are in a state of active development contain any notable proportion of laccase.

In dealing with roots, rhizomes, tubers, and parenchymatous fruits, the juice may be precipitated with alcohol immediately after its extraction, but, in the case of green organs, the juice should be saturated with chloroform and allowed to remain for 24 hours, when it will coagulate spontaneously, and only the filtered liquid is treated with alcohol.

C. H. B.

Asparagine in the Roots of *Nelumbo Nucifera*. By Y. KINO-SHITA (*Bull. Coll. Agric., Imp. Univ., Tokyo*, 1895, 2, 203—204).—The root of *Nelumbo nucifera* is rich in starch, and is used in Japan, in the boiled condition, as food. The following analytical results were obtained by Kellner:—water, 85·84; the dry substance gave: crude protein, 7·75; fat, 1·44; fibre, 7·19; non-nitrogenous extract, starch, &c., 78·59; ash (free from carbon and carbonic anhydride), 5·03 per cent.

Asparagine has been detected in comparatively few roots; the roots of *Althæa* contain 2, of *Glycyrrhiza* (Plisson), 0·8, of *Scorzonera* (Gorup), 0·6, and potatoes (Schulze), 3 per cent. The dry substance of *Nelumbo* yielded nearly 2 per cent. of asparagine.

N. H. J. M.

Occurrence of Cytisine in various Papilionaceæ. By PIETER C. PLUGGE (*Arch. Pharm.*, 1895, 233, 430—441).—Cytisine is contained in the following Papilionaceæ:—(1) *Cytisus Laburnum*, L., (*Laburnum vulgare*, Grisebach); (2) *C. alpinus*, Mill; (3) *C. supinus*, Jacq.; (4) *C. elongatus*, W. u. K.; (5) *C. Weldinii*, Vis; (6) *C. sessilifolius*, L.; (7) *C. hirsutus*, L.; (8) *C. biflorus*, L'her; (9) *C. Alsingeri*, Vis; (10) *C. nigricans*, L.; (11) *C. proliferus*, L., fil.; (12) *Cytisus Adami*, Poit; (13) *C. ratisbonensis* β -minor, Schäf; (14) *C. ratisbonensis*, Schäf; (15) *C. polytrichus*, M. B.; (16) *Genista racemosus*, Marnoch; (17) *G. ramosissimus*, Ten; (18) *G. Spicatus*; (19) *Ulex europæus*, L. (Gerrard's *Ulexine*); (20) *Sophora speciosa*; (21) *S. tomentosa*; (22) *S. secundiflora*, Lagasca; (23) *Baptisia tinctoria* (v. Schroeder's baptitoxime); (24) *B. Australis*; (25) *Euchresta Horsfieldi*, Benn. The following members are free from cytisine:—(1) *Cytisus nigricans*; (2) *C. sessilifolius*, L.; (3) *C. argenteus*, L.; (4) *C. capitatus*, Jacq.; (5) *Genista tinctoria*, L.; (6) *G. pilosa*, L.; (7) *G. anglica*, L.; (8) *G. germanica*; (9) *Sophora japonica*, Dc.; (10) *S. japonica pendula*; (11) *Sophora affinis*. The author has in-

vestigated Nos. 20—25 in the first class, and Nos. 9—11 in the second. *Sophora speciosa* contains cytisine to the extent of 3·23 per cent., and as the infusion of the seeds is identical with cytisine in physiological action, the presence of a second alkaloid is improbable. These results confirm the author's previous statement that Wood's "sophorine" and cytisine are identical. *S. secundiflora*, Lagasca (*Virgilia secundiflora*, Cad.), also contains in its seeds 3·47 per cent. of cytisine. The alkaloid in the seed of *Euchresta Horsfieldii*, Benn, was identified by means of its colour reactions and the analysis of its auro- and platino-chlorides, as cytisine. Cytisine gives, in addition to the reactions already known, a violet-red coloration with concentrated sulphuric acid and potassium permanganate, the intensity of the violet tint gradually increasing.

J. B. T.

Composition of Pure Fruit Juices. By H. KREMLA (*Bied. Centr.*, 1895, **24**, 498; from *Zeit. f. Nahrungsmittelhygiene u. Warenkunde*, **7**, 365—370).—The juices of the following fruits were analysed: (1) cherry; (2) currant; (3) gooseberry; (4) cranberry; (5) cider apple; and (6) melon. The results are given in grams per litre of juice. The acid is calculated as malic acid, and the sugar (reducing) as invert sugar.

	Balling's extract.	Acid.	Sugar.	Nitrogen.	Ash.
1	166·0—266·8	3·13—7·23	100·6—172·6	—	—
2	108·0—167·1	21·2—23·8	48·5—86·8	0·248—0·711	3·56—7·58
3	91·1	13·1	59·7	0·098	2·68
4	119·0	22·7	74·5	—	2·44
5	169·5	11·07	104·1	—	—
6	99·5	1·73	41·4	—	—

	K ₂ O.	CaO.	MgO.	P ₂ O ₅ .
2	2·128—2·549	0·206—1·230	0·106	0·229—0·501
4	1·192	0·270	0·126	0·099

The sp. gr. were as follows: (1) 1·0639—1·1023; (2) 1·0400—1·0644; (3) 1·0355; (4) 1·0462; (5) 1·0653; (6) 1·0387. Black cherries gave much more sugar and extract than red ones. Benzoic acid was found in cranberry juice.

N. H. J. M.

Bark and Leaves of *Drimys Granatensis*, L. By OSWALD HESSE (*Annalen*, 1895, **286**, 369—376).—The statement that the bark of *Drimys Granatensis* contains cotoïn has led the author to submit it to examination, the leaves having been included in the investigation, the result of which shows that cotoïn is not present in either bark or leaves. Three new substances have been isolated, drimin, drimyssic acid, and drimol.

Drimin, $C_{13}H_{14}O_4$, is obtained from the pulverised bark, which is extracted with ether, the ethereal solution evaporated, and the residue extracted with boiling petroleum; the insoluble portion is then dissolved in ether, and light petroleum added, when an oil is thrown down. On evaporating the solution and dissolving the residue in alcohol, ether precipitates drimin, which separates from alcohol as a micro-crystalline powder of pale brown colour; it melts at 256° .

Drimyssic acid has not been characterised; it was obtained from the liquid filtered from drimin, and has the properties of an acid.

Drimol, $C_{28}H_{58}O_2$, is obtained from the leaves by extracting with ether, evaporating the solvent, and dissolving the residue in alcohol; it crystallises from alcohol in small, white needles, and melts at $73-74^\circ$. The *acetyl* derivative, $C_{28}H_{57}AcO_2$, crystallises in small, white leaflets, and melts at $42-43^\circ$. The action of hydriodic acid (sp. gr. = 1.7) gives rise to the *iodide*, $C_{28}H_{57}IO$, which crystallises from hot glacial acetic acid in small needles; by the action of alcoholic potash, drimol is regenerated.

M. O. F.

Amount of Fat, Sugar and Tannin in Coffee. By E. HERFELDT and ALBERT STUTZER (*Zeit. angew. Chem.*, 1895, 469—471).—The fat, or rather the ethereal extract, of coffee seems to be much increased by the roasting process; a sample of Santos coffee gave on analysis 10.86 per cent. of water and 8.15 per cent. of fat, whilst after roasting it yielded 2.43 per cent. of water and 16.58 per cent. of fat. New Granada coffee showed 10.45 of water and 13.10 per cent. of fat; after roasting, 2.18 per cent. of water and 15.44 per cent. of fat. Java coffee, however, showed a large decrease in fat, its moisture and fat being respectively 10.05 and 14.00 per cent. before, but 2.96 and 11.30 per cent. after roasting. The iodine and saponification figures of the fat before or after roasting do not admit of any definite conclusions.

The authors have not been able to detect actually existing sugars, but a little may be formed by hydrolysis of the tannin under favourable conditions. As regards the caffetannic acid, the authors have not been able to get anything like trustworthy results by estimating the sugar formed on hydrolysis with tartaric acid; treatment with aqueous soda also failed. Experiments to isolate the tannin as a bromo-derivative also proved unsatisfactory.

L. DE K.

Composition of *Pachyma Cocos* and *Mylittia Lapidescens*. By ERNST WINTERSTEIN (*Arch. Pharm.*, 1895, 233, 398—409).—Two specimens of *Pachyma Cocos* gave the following analytical results:—Protein substances = 0.56—1.00; substances allied to chitin = 0.60—1.00; ethereal extract = 0.35—0.42; ash = 0.06—0.25; water = 16.86—12.09; *d*-glucose = 1.40—1.13; fungus-cellulose = 2.25—3.24; pachymose = 76.21—79.84 per cent. The ethereal extract probably consisted of cholesterol. Gummy matters are also present in small quantity. Pachymose is an anhydride of *d*-glucose similar to parадextran and paraisodextran; when hydrolysed it yields 97 per cent. of *d*-glucose. The low content of ash is noteworthy. *Mylittia lapidescens* is composed as follows:—Protein sub-

stances = 2.36; substances allied to chitin = 0.91; ethereal extract = 0.10; ash = 0.20; water = 4.56; fungus-cellulose = 2.80; saccharo-colloides = 88.98 per cent. No carbohydrate soluble in cold dilute alkali is present; after prolonged heating with alkali, a slimy substance was isolated, which is similar to Tollens's saccharo-colloides. Full details of the analytical methods are given. J. B. T.

Kola Nut. By G. LE BON (*Exper. Stat. Record*, 1895, **7**, 148; from *U.S. Consular Rep.*, 1895, Apr., 537—540).—The fresh kola nut possesses remarkable stimulating powers, whilst the dried nuts do not. It contains caffeine (2.35 per cent.), theobromine (0.023 per cent.), and a red glucoside (1.3 per cent.), which after mastication is largely transformed into caffeine. Experiments with caffeine and theobromine showed that when mixed in the proportions in which they occur in the nuts, their sustaining power is equal to that of the nuts; neither compound alone has so great a stimulating effect as the nuts. It is thought that the nuts are of extreme importance as a muscular stimulant. N. H. J. M.

Coco-nut Shells. By R. W. TROMP DE HAAS and BERNHARD TOLLENS (*Annalen*, 1895, **286**, 303—306).—The hard, inner shells of coco-nuts were finely powdered and extracted successively with cold, dilute hydrochloric acid, cold dilute ammonia, boiling alcohol, and boiling ether. The dry powder was then heated for an hour on the water-bath with 10 parts of 4 per cent. sulphuric acid, and subsequently in a porcelain basin over the flame; the hot, filtered liquid was neutralised with calcium carbonate, and evaporated, yielding a syrup which was re-dissolved in alcohol. This solution deposited 8 grams of xylose, 110 grams of the powdered shells having been employed. The specific rotatory power of the sugar thus obtained was $[\alpha]_D = +64.8^\circ$ seven minutes after solution, diminishing to $[\alpha]_D = +18.3^\circ$ on the following day. The xylose obtained from coco-nut shells crystallises from alcohol in white needles, and is not associated with other sugars.

The portion of shell-powder which remained undissolved by the hydrolytic agent, was treated with a mixture of 10 parts of concentrated sulphuric acid and two parts of water. After $2\frac{1}{2}$ days, the liquid was diluted with 5 litres of water, and boiled for five hours in a reflux apparatus, filtered, and neutralised with calcium carbonate. The alcoholic solution of the syrup obtained on evaporation did not give the reaction for pentoses, but yielded pure *d*-glucose, which had a specific rotatory power $[\alpha]_D = +50.8^\circ$, after remaining in solution for a day. Twenty grams of the powder undissolved in the first operation yielded 0.5 gram of *d*-glucose. M. O. F.

Composition of some French and other Oats harvested in 1893. By BALLAND (*Compt. rend.*, 1895, **120**, 502—504).—Various samples of oats from known sources were examined in order to be able to identify the principal types offered in the French markets. The War Department excludes nearly all foreign oats from their stores.

As regards chemical composition, the grey or black oats of Beauce contained over 10 per cent. of proteïds, about 5 per cent. of fat, and 7·5 to 9 per cent. of cellulose; the composition of samples from Champagne, Picardie, Vosges (except cellulose over 9 per cent.), Sweden, and of white Norwegian oats was similar. Russian oats (grey or black) contained: proteïds 10, fat less than 4, and cellulose 11 per cent. United States oats: proteïds 10, fat 5 per cent. Algerian oats: proteïds less than 9·5, fat 5 per cent. White oats from St. Petersburg contained 14 per cent. of proteïds; other white Russian oats: proteïds over 10, fat 3—4 per cent., and an excess of cellulose. The weight of the grains per thousand, which varies very considerably, is given in most cases, and also the percentages of kernel.

N. H. J. M.

Cuscuta Epithymum. By GASTON BARBEY (*J. Pharm.*, 1895, [6], 2, 107—112).—The common dodder is a parasitic plant of the order *Convolvulaceæ*, and is said to possess diuretic and laxative properties, and to be a specific for gout. The author has examined the extract from 2 kilos. of the plant. The aqueous extract is acid, and yields a precipitate with potassium hydrogen carbonate, from which a yellow, amorphous powder, cuscutin, is extracted by ether. It is also precipitated by dilute sulphuric acid, and the residual solution then reduces alkaline copper tartrate. The alcoholic extract of the residue from the aqueous extract, yields a further quantity of cuscutin. Resinous and fatty products were also isolated, together with a tannin and a small amount of a crystalline substance, having a faint odour of coumarin.

Cuscutin is insoluble in cold water, and only sparingly soluble in boiling water yielding a yellow solution, from which it is precipitated in the amorphous form on cooling; with concentrated sulphuric acid, it gives a reddish-brown solution, having a green fluorescence; it is also soluble in acetic acid without change of colour. With ferric chloride, the aqueous solution gives a characteristic and very delicate violet-grey turbidity, red by transmitted light. *Cuscutin* is very soluble in alkalis, giving yellow solutions, which dye silk and paper, and stain the skin. *Cuscutin* is hydrolysed by mineral acids yielding glucose, and a resinous substance, *cuscuretin*, and it is, therefore, a glucoside. No analytical data are furnished.

JN. W.

Preparation and Composition of Tofu. By M. INOUE (*Bull. Coll. Agric., Imp. Univ., Tokyo*, 2, 209—215).—In order to make up the deficiency of proteïds in rice, the inland inhabitants of Japan utilise various leguminous seeds, especially the soja bean. Two products prepared from this bean, miso and natto, have already been described (Kellner, *Tokyo Bull.*, 1, No. 6; and Yabe, *Abstr.*, 1895, ii, 130). A third preparation of soja beans, tofu, is obtained by pulping the beans after soaking them for 12 hours in water, boiling with water (3 parts) for an hour and filtering through cloth; the liquid which resembles milk in appearance, and fresh malt in taste, has a neutral or slightly acid reaction, but after several days becomes strongly acid (lactic acid), when the separation of casein takes place. In

manufacturing tofu, the fresh filtrate is treated with about 2 per cent. of concentrated sea-water, the flocculent precipitate slowly pressed, and cut into tablets; the product has the taste of milk casein. In the beans themselves, the casein is in a soluble form in combination with potassium or sodium, and is not coagulated by boiling, but is precipitated by the calcium and magnesium salts in the brine; when tofu is boiled with 1 per cent. aqueous disodium phosphate, the casein redissolves, yielding an opalescent solution, calcium phosphate being formed.

Tofu is sometimes subjected to the action of frost, when it contracts and loses a large amount of water; the product is called koridofu. The following numbers show the percentage composition of (1) the fresh milky liquid, (2) tofu (Kellner), (3) koridofu, and (4) yuba (prepared by evaporating the soja bean extract):—

	Water.	Proteids.	N-free extract.	Fat and lecithin.	Cellulose.	Ash.
1	92.53	3.02	1.88	2.13	0.03	0.41
2	89.29	4.87	4.35	—	—	0.48
3	15.32	41.42	15.05	23.65	1.48	3.08
4	21.85	42.60	7.65	24.6	—	2.82

The milky extract left for two weeks contained 0.092 gram of lactic acid per 100 c.c. The dry tofu yielded 11.2 per cent. of lecithin.

According to Osawa, tofu is as readily digested as beef.

N. H. J. M.

Action of Lime and Magnesia on the soluble Phosphoric Acid of the Soil. By C. SCHREIBER (*Exper. Stat. Record*, 1895, 7, 104, from *Rev. Agr. Louvain*, 1895, 4, 66—69).—Two mixed manures one containing dicalcium phosphate, calcium sulphate and magnesium carbonate, the other sodium phosphate, and calcium and magnesium carbonates were applied to oats (to be followed by turnips) on sandy, humus and loamy soils. In each case, the first named mixture gave much higher results, the difference being most marked in the case of turnips; this seems to be due to the calcium and magnesium carbonates of the second mixture rendering the phosphoric acid of the sodium salt insoluble; the action would be more complete during the second crop. The results of experiments on humus soil confirmed the author's previous conclusions, that the phosphoric acid combined with the humus of peaty soils, which is readily soluble in alkaline ammonium citrate, is almost useless for vegetation. In some cases, humus acts on assimilable phosphoric acid in a manner analogous to calcium carbonate.

N. H. J. M.

Assimilable Nitrogen and its Transformations in Arable Soil. By PAGNOUL (*Compt. rend.*, 1895, 120, 812—815).—A number of experiments were made in which large cases were filled with soil, (60 kilos.), variously manured, some of which were exposed, others sheltered from rain; all the cases were kept free from vegetation. An examination of the soil showed that the organic nitrogen is first transformed into ammonia, next into nitrous acid and finally into nitric acid.

The loss of nitrogen from bare soil may be considerable during heavy rains, but is entirely stopped by vegetation, such as grass. The application in August of carbon bisulphide (10 c.c.) to soil (2 kilograms) manured with cake, entirely checked nitrification until the end of September, but by the 16th October, 0.017 per cent. of nitric nitrogen was found; in a similar experiment without carbon bisulphide there was considerable nitrification during September. The effect of carbon bisulphide was therefore not to destroy the nitrifying organism, but to paralyse it temporarily; ammonia was produced during this time in considerable quantity amounting to 0.027 per cent. by the 15th October. N. J. H. M.

Behaviour of Hippuric Acid in Soils. By K. YOSHIMURA (*Bull. Coll. Agric., Imp. Univ.*, 2, 221—223; *Note* by OSCAR LOEW, 223—224).—Of the total nitrogen of cow's urine, about 10 per cent. is in the form of hippuric acid, of horse's urine, about 2 per cent. Experiments were made to ascertain the absorptive power of soils for hippuric acid. The soils, one consisting of volcanic ashes and loam, the other a clayey soil, were found to have no power of retaining either the free acid or its sodium salt.

Dilute solutions of sodium hippurate containing potassium phosphate and magnesium sulphate, are able to develop mould fungi and microbes.

Solutions of sodium hippurate infected with surface and sub-soils were decomposed, ammonia being liberated; the decomposition is more rapid under the influence of surface soil than of subsoil organisms; only in one experiment was there an indication of nitrous acid with Griess' reaction.

Loew points out that the absence of nitrification in solutions of sodium hippurate is in accordance with other similar observations. Sterilised solutions of ammonium formate and oxalate respectively (0.05 per cent.), with potassium phosphate and magnesium sulphate, were infected from a culture from garden soil; the formate yielded no nitrate, and the oxalate only a small amount, about one-tenth the quantity yielded by ammonium carbonate. Nitrification is nearly twice as quick in the dark as in daylight.

There exists a bacillus (*B. methylicus*) able to assimilate formates (*Centr. f. Bact.*, 12, No. 14). N. H. J. M.

Effect of Carbon Bisulphide on exhausted or "sick," (fatigués) Soils. By C. OBERLIN (*Exper. Stat. Record*, 1895, 7, 88—89; from *Journ. Agr. Pract.*, 1895, 59, 459—464, 499—503, 535—540).—In applying carbon bisulphide for grape phylloxera, holes, 50—60 cm. deep, are made in the soil by means of iron rods, carbon bisulphide (50—100 c.c.) poured in and the holes carefully plugged. The vines are generally removed, and other crops grown for six years. As compared with crops growing on soils not treated with carbon bisulphide, those grown on soil so treated, were in many cases decidedly superior, for example, oats, lucerne, hairy vetch and beans; lucerne was especially benefited; on soil not treated with bisulphide, the crop

still failed after six years, parallel plots to which there had been an application yielding vigorous growth. N. H. J. M.

Saline Soil and Water from Persia. By KONRAD NATTERER (*Monatsh.*, 1895, **16**, 639—673).—The author gives an account of the composition and properties of the samples of soil and water brought from the steppes of south-west Persia by Otto Stapf. In most cases, the samples contained those salts which are present in sea-water and in somewhat the same proportion, and the author therefore concludes that the salt wastes have been formed by the evaporation of salt water which has been separated from the main body of the ocean by the raising of the level of the land in earlier geological times. G. T. M.

The Potash and Phosphoric Acid required by Cultivated Plants. By SMETS and C. SCHREIBER (*Exper. Stat. Record*, 1895, **7**, 107—108; from *Rev. Agr. Louvain*, 1895, **4**, 78—79).—The relative requirements of various plants for potash and phosphoric acid are as follows:—For potash: oats (native) 18, oats (Flanders) 23, potatoes 37, spring wheat 43, flax 56, mustard 70, turnips 80. For phosphoric acid: lupins 27, potatoes 50, mustard 53, spring wheat 60, oats (native) 64, flax 66, oats (Flanders), 75, turnips 85.

The results were furnished by 267 pot experiments.

N. H. J. M.

Value of Bone Phosphates. By ULBRICHT (*Bied. Centr.*, 1895, **24**, 478—479; from *D. agrik.-chem. Vers.-Stat., Dalme*, 3—8).—The effective value of a bone phosphate depends on the amount of available phosphoric acid in the soil. The results of experiments in which four kinds of soil were manured, partly with bone phosphates and partly with superphosphate, showed the following increase in dry produce, due to superphosphate, as compared with the yield after the application of bone phosphates. Increase on light soil 10, on soil poor in phosphates 25, on artificial soil made of quartz, sand, and kaolin, and free from phosphates, 294, and on soil exhausted by vegetation, 2½ per cent. Bone meal may, under favourable conditions, have a considerable effect even when employed in the spring; but its action is much hindered by dry weather, especially if it is not sufficiently finely ground. N. H. J. M.

Citrate Solubility of Basic Slag as Expressing its Manurial Value. By PAUL WAGNER (*Bied. Centr.*, 1895, **24**, 480; from *Deut. landw. Presse*, 1894, 983—984).—There is no regularity in the relation of the percentage of free lime in basic slag and its citrate solubility, as is stated by Hoyermann (*Bied. Centr.*, **24**, 130). As regards Hoyermann's explanation of the increased citrate solubility of slags rich in lime after fusion with sand, the author is of opinion that the calcium silicate formed during the fusion forms a readily decomposable calcium silicate-phosphate with the calcium phosphate of the slag.

N. H. J. M.

Chlorine in Rain Water. By N. PASSERINI (*Ann. Agron.*, 1895, 21, 399—400; from *Bol. Scuola. agron. Scandici*, 1893, 12—22).—The following average amounts of chlorine in parts per million were found.

	Spring.	Summer.	Autumn.	Winter.
1890.....	5.1	7.0	6.5	8.3
1891.....	3.4	4.5	3.6	3.2

The station is situated near Florence, all the wind coming from the sea except the north-west; the gauge is 75 kilom. from the west coast, and 107 kilom. from the Adriatic.

At Antignano, near Leghorn, the average amount of chlorine in the rain is 116 parts per million. N. H. J. M.

Losses of Nitrogen in Waters of Infiltration. By J. J. THEOPHILE SCHLOESING (*Compt. rend.*, 1895, 120, 526—530).—A number of samples of water were taken from French rivers at different points, and the nitric nitrogen determined. The samples were taken during the last prolonged frost, after the temperature had been considerably below zero for many weeks, during which the rivers could not have been fed by surface, but only by subterraneous, water; aquatic vegetation, which would otherwise take up nitrates from the rivers, was, it is thought, practically suspended for the time.

The results are given in parts per million.

Seine in Paris, Feb. 9th,	2.09	13th,	2.31	19th,	2.25	23rd,	2.26.
„ in Montereau, 16th Feb.,	1.99	27th Feb.,	2.08.				
„ in Charenton, 15th Feb.,	2.55	28th Feb.,	2.75.				
Marne, Charenton, 14th Feb.,	2.34	28th Feb.,	2.02.				
Yonne, Monteneau, 16th Feb.,	2.21	27th Feb.,	2.52.				
Oise, Pontoise, 19th Feb.,	2.78	1st March,	2.43.				
Vanne,		4th March,	2.61.				
Dhuis,		8th March,	2.86.				
Avre,		7th March,	3.08.				

Bousingault determined nitrates in Seine water (Paris) in 1856–57, but obtained much lower results (*Agronomie*, 2, 65).

The chief point of interest shown by the above results is the uniformity in the amount of nitrates at the different dates, notwithstanding that the amount of water was reduced, at the later dates, to at least half.

From the average amount of nitric nitrogen (2.42 per million) the total annual loss per hectare is calculated for the basin of the Seine from the supposed amount of drainage. If the drainage is one-sixth of the total rainfall (700 mm.), the loss per hectare of nitric nitrogen would be 2.8 kilos.; if one-fourth, 4.29 kilos.; and if one-third, 5.65 kilos. The loss would, however, be mainly from arable land, and not from woods, and meadows, &c. When calculated on arable land and vineyards alone, the loss (in the basin of the Seine) is found to be 4.2, 6.44, or 8.48 kilos. per hectare, according to the amount of drainage. The calculations, which are only provisional, indicate much less loss than was generally supposed to take place.

N. H. J. M.

Analytical Chemistry.

New Forms of Gas Burettes. By O. BLEIER (*Ber.*, 1895, **28**, 2423—2427).—In order to avoid inaccuracy in measuring the original volume of gas taken, the burette is made to contain exactly 100 c.c. under the conditions of experiment. The burette is filled with water, and the gas introduced through a tap at the top by allowing the water to run out by a tap at the bottom of the burette. If the gas is readily soluble in water, it must be passed through the burette for a certain time, in no case more than 30 seconds, in order to saturate the moisture adhering to the walls. A. H.

Inertness of Oxidising and Reducing Agents in Analyses in the Wet Way. By MARCELLIN BERTHELOT (*Ann. Chim. Phys.*, 1895, [7], **4**, 429—432).—The author calls attention to the fact that in the titration of persulphuric acid with ferrous sulphate and sulphuric acid, a discoloration of the liquid often occurs, and the final point is difficult to detect. This leads to erroneous results, and the cause is, probably, that an intermediate compound of persulphuric acid with ferrous sulphate is formed; this has a most decided colour, is unstable, but is not instantaneously reduced. In cases of titration of persulphuric acid, it is, therefore, better to at once add an excess of ferrous sulphate, and then to titrate back again with permanganate.

Titration of oxalic acid with potassium permanganate in similar manner, proceed very slowly in the cold, but, in order to complete the reduction quickly, it is merely necessary to add a trace of manganese sulphate. A similar observation has also been made by Engel (*Abstr.*, 1892, 277). These results may be due to the temporary formation of a manganic salt, or to the union of permanganic acid with a manganese salt. J. J. S.

Estimation of Water in Commercial Ammonium Sulphate. By JOHN HUGHES (*Chem. News*, 1895, **72**, 6).—The author calls attention to the importance of always estimating the moisture, and also the free sulphuric acid, in the samples. The water should be estimated by drying at 100°, and this should be done first in the original sample, and then be repeated after the salt has been finely ground for the purpose of analysis, as the moisture lost during the preparation of the sample may occasionally amount to 1 per cent. The analytical results are afterwards calculated into the state of the sample as received. L. DE K.

Detection of Chlorine, Bromine, and Iodine in Organic Compounds. By P. N. RAIKOW (*Chem. Zeit.*, 1895, **19**, 902—903).—A fragment of silver nitrate is for a moment gently heated with a little sulphuric acid in a test tube. After cooling, the substance to be tested is added, and the mixture is again gently heated. If iodine is

present, part of it escapes, but some of it forms a yellow precipitate of silver iodide, which, however, gradually disappears on boiling.

Chlorine will be detected by a temporary white precipitate; bromine by a temporary pale yellow deposit. The process is applicable to all organic compounds containing haloids. L. DE K.

Electrolytic Estimation of the Halogens. By GEORG VORTMANN (*Monatsh.*, 1895, **16**, 674—683).—The author has previously described a method for the electrolytic estimation of iodine (*Abstr.*, 1894, ii, 426), and now calls attention to several important improvements in the process. An anode of pure silver, shaped like a clock-glass, a cathode of platinum or copper, and a current which does not exceed 2 volts in the case of cold solutions containing no alkali tartrate, or 1.3 volts when the solution is warm and contains alkali tartrates, are employed. The electrolysis is continued until the solution no longer gives the iodine reaction or until a new anode placed in the solution does not gain in weight. Under these conditions, no silver is dissolved from the anode, which retains on its surface the whole of the iodine in the form of silver iodide. G. T. M.

Estimation of Iodine in Organic Substances. By M. C. SCHUYTEN (*Chem. Zeit.*, 1895, **19**, 1143).—The author's method is applicable to members of the fatty series only. The substance is introduced into a 15-cm. test tube, and mixed with finely powdered, previously fused, potassium dichromate. After covering the mixture with another 5—6 cm. layer of the chromate, the tube is drawn out to a bent capillary. While the latter is kept cool with a wet piece of cloth, the contents of the tube are heated, commencing at the top, until no further sublimation of iodine takes place.

The tube is cut in two, the part containing the iodine is rinsed with a solution of potassium iodide, and the iodine is then titrated as usual; or the iodine may be weighed. In the latter case, the capillary part containing the iodine is connected with a calcium chloride tube containing also a few pieces of soda-lime; when a magnifying glass no longer shows the presence of water, the tube is weighed. After gently heating to volatilise the iodine, the glass is re-weighed.

L. DE K.

Estimation of Sulphur in Pyrites. By ALEXANDER VON ASBÓTH (*Chem. Zeit.*, 1895, **19**, 598—599).—The author has investigated the processes recommended by Johnson (reduction of the ferric salt by means of sodium hypophosphite before precipitating with barium chloride), Hoehnel and Glaser (fusion with sodium carbonate and sodium peroxide), and Fresenius (fusion with sodium carbonate and potassium nitrate).

The second method is, in the author's opinion, the best, but it is necessary to evaporate the aqueous solution to dryness with addition of bromine and hydrochloric acid so as to ensure the complete oxidation of the sulphur and the removal of any silica. L. DE K.

Detection of Sulphates, Sulphites, and Thiosulphates in Presence of each other. By R. GREIG SMITH (*Chem. News*, 1895,

72, 39—40).—Excess of barium chloride and plenty of ammonium chloride are added to the solution, which is made dilute when thiosulphates are present; hydrochloric acid is then dropped in until barium sulphate alone remains undissolved. The filtered solution is next rendered permanently yellow with iodine, when a turbidity or precipitate indicates the presence of sulphite, which has been oxidised to sulphate, whilst any thiosulphate is converted into tetrathionate; this in its turn is oxidised to sulphate on adding bromine water to the clear solution. Hydrogen sulphide would interfere with these reactions, and is removed at the start by means of a current of carbonic anhydride.

D. A. L.

Qualitative Analysis of a Mixture of Hydric Sulphide, Polysulphide, Thiosulphate, Sulphite, and Sulphate. By W. POPPLEWELL BLOXAM (*Chem. News*, 1895, 72, 63—64).—The solution is precipitated with an ammoniacal solution of zinc, cadmium, and ammonium chlorides. The filtrate is divided into two portions; one of these is tested for sulphites and thiosulphates by Fresenius's process, which consists in neutralising part of the liquid with acetic acid and adding a trace of sodium nitroprusside and, if necessary, some potassiumferrocyanide, which gives a red coloration with sulphites. Thiosulphates are tested for by adding hydrochloric acid. The other half is tested for sulphates as follows. After adding a little sodium hydrogen carbonate, the liquid is placed in a flask fitted with a treble perforated cork; through an inlet tube, a current of carbonic anhydride is admitted, and an outlet tube is provided dipping below the surface of water, whilst through the third hole, a small stoppered separating funnel is passed, the tube reaching nearly to the bottom of the flask. While the gas is passing, the liquid is gradually raised to boiling, and, after all the air is expelled, hydrochloric acid is slowly admitted through the funnel until it is in excess; the liquid is then boiled down to one-fifth of its original bulk, the current of carbonic anhydride still being maintained. After filtering off the separated sulphur, the liquid is tested for sulphates as usual.

L. DE K.

Estimation of Organic Nitrogen by the Kjeldahl Process. By HENRI E. CAUSSE (*J. Pharm.*, 1895, [6], 1, 543—549; compare Dyer, *Trans.*, 1895, 811).—The ordinary modification of the Kjeldahl process yields satisfactory results with substances, such as guano, containing less than 5 per cent. of nitrogen, but with more highly nitrogenous substances, such as wool and leather, it gives results as much as 2 per cent. too low. The addition of mercuric oxide, recommended by the American Committee, is either unnecessary or objectionable, for, although the time required to effect the decolorisation of the liquid may be considerably diminished by using sufficient oxide, the clear product then contains unreduced nitrogen. A sample of dried wool, for instance, which yielded about 12·5 per cent. of nitrogen by the soda-lime method, and also by the American method when a small amount of the oxide (0·2—0·3 gram to 0·3—0·35 gram of wool) was used, gave only 10·5 per cent., or even less, when the amount

of the oxide (2—4 grams) was such as to effect decolorisation in an hour.

Neither is the result improved by the addition of sodium sulphide to the alkaline liquid before distillation, and the deficiency is therefore not due to the retention of ammonia in mercuric combination; the addition of permanganate is equally inefficacious, as nitrogen ring compounds are stable towards that agent.

The author recommends the substitution of copper sulphate for the mercury or mercuric oxide. The substance (0.3—0.8 gram) is boiled in a round-bottomed flask with concentrated sulphuric acid (20 c.c.), and a small amount (0.3 gram) of the sulphate, until a clear solution is obtained; the operation requires about three hours, but does not need attention if the flask is surrounded by a metal jacket. The product is diluted (to 300 c.c.), rendered alkaline with caustic soda, and distilled into standard sulphuric acid in the usual way. The copper remains in the solution, which is at first blue, and finally colourless, provided the caustic soda is free from carbonate, but if carbonate is present copper is precipitated, and a portion of the ammonia retained.

The specimen analyses quoted agree well with duplicates made by the soda-lime method. JN. W.

Estimation of Phosphoric acid by the Molybdenum Method.

By HUGO NEUBAUER (*Zeit. anorg. Chem.*, 1895, 10, 60—65).—In the estimation of phosphoric acid by means of molybdic acid, the precipitate obtained is usually not more than 0.27 gram $\text{Mg}_2\text{P}_2\text{O}_7$. The author has determined the correction necessary to compensate for the volatilisation of phosphoric acid. With 0.07 gram $\text{Mg}_2\text{P}_2\text{O}_7$, the volatile $\text{P}_2\text{O}_5 = 0$; with 0.35 gram $\text{Mg}_2\text{P}_2\text{O}_7$ the volatile P_2O_5 calculated as $\text{Mg}_2\text{P}_2\text{O}_7 = 0.006$ gram. Whence the following equation is obtained for the correction number x . When $n =$ the $\text{Mg}_2\text{P}_2\text{O}_7$ found in milligrams, $x = (n - 70) \cdot 0.021$.

The author recommends the use of a crucible lid coated with magnesium oxide to prevent loss of phosphoric acid, especially when larger quantities of phosphoric acid are being estimated. The following directions must be closely followed in order to obtain trustworthy results by the molybdic acid method. The yellow precipitate is dissolved in 100 c.c. of $2\frac{1}{2}$ per cent. ammonia. The precipitation with the magnesia mixture must be performed slowly, with stirring. When the volatile phosphoric anhydride is determined directly by means of a crucible lid coated with magnesia, the filter is burned at the lowest possible temperature, and the lid put on directly the temperature is raised, the precipitate being heated for one hour over a strong Terquem- or Teclu-burner, in such a way that the whole crucible is at a full red heat. Care must be taken to determine if the magnesia coated lid gains in weight under the influence of the burning gas. The author recommends a spirit burner instead of gas, especially when the gas contains any quantity of sulphur compounds.

E. C. R.

Analysis of Artificial Manures. By VON GRUEBER (*Zeit. angew. Chem.*, 1895, 504—516).—An elaborate article, dealing with the practical analysis of manures in the way proposed by the society of German manure manufacturers. The methods present, on the whole, no novel features, but, by strictly adhering to them, analytical differences will, no doubt, be to a great extent obviated. L. DE K.

Gravimetric Estimation of Arsenic. By CARL FRIEDHEIM and PAUL MICHAELIS (*Zeit. anal. Chem.*, 1895, **34**, 505—545).—I. *The ammonium magnesium arsenate method.*—The authors, combining the most advantageous features of the proposals of Puller, Wood, Fresenius, and others, proceed as follows:—About 0.3 gram of arsenic acid in 100 c.c. is mixed with 10 c.c. of ammonia (sp. gr. 0.96), 20 c.c. of magnesium mixture (made from magnesium chloride), and about 45 c.c. of alcohol; after 48 hours, the precipitate is collected and washed with a mixture of 2 vols. alcohol, 1 vol. ammonia, and 3 vols. water until free from chlorine. The filtrate contains only unweighable traces of arsenic, so that Puller's correction of 1 milligram per 16 c.c. is not required. The use of the Gooch crucible, with a filter-bed of asbestos, is strongly recommended, since, with paper filters, a loss of arsenic is inevitable. The precipitate is ignited in oxygen, at first by a single burner, then by a multiple one for 15—30 minutes, until a constant weight is attained; the blowpipe should not be used, for, at the temperature which it gives, decomposition of the pyroarsenate and loss of arsenic occur, moreover, the crucible should stand in a small porcelain capsule to protect its contents from the flame. The precipitate undergoes partial decomposition when heated with water, hence attempts to ascertain its weight by rinsing it into a crucible and evaporating the water results in serious loss. Bunsen's method of dissolving in nitric acid and evaporating is also unsatisfactory, but experiments conducted as above did not in any case deviate more than 0.0007 gram of As_2O_3 from the amount taken.

II. *Estimation as Trisulphide.*—Here, also, the employment of the Gooch crucible avoids the inconveniences attending the use of dried paper filters. The chief difficulty in this process is the tendency of the precipitate to contain more sulphur than corresponds with the formula As_2S_3 ; part, at least, of this excess, is shown to exist in the form of arsenious hydrosulphide, which compound is not decomposed by expelling the dissolved hydrogen sulphide by a current of carbonic anhydride, and is only very slowly decomposed, with partial oxidation and separation of sulphur, when the precipitate is dried at 100—103°. Hence, all attempts to dissolve out the excess of sulphur by carbon disulphide, fail to remove it completely. For the same reason, also, the method of Classen and Ludwig (*Abstr.*, 1885, 932) does not give correct results. Mohr's method of dissolving in ammonia and evaporating the solution is also untrustworthy, as, in consequence of the large surface exposed, oxidation of sulphur and loss of weight occur during the drying. Rose's method of oxidising the precipitate, determining the total sulphur as barium sulphate, and estimating the arsenic from the difference, seems to be free from sources of error. A customary method is to oxidise the precipitate by nitric acid and

throw down the arsenic acid as ammonium magnesium arsenate, but the presence of the sulphuric acid resulting from the oxidation, entails the co-precipitation of some basic magnesium sulphate, and renders a double precipitation necessary. In this second precipitation, too much dilution must be avoided; 30 c.c. of solution for 0.1 gram of As_2O_3 is an appropriate proportion; a little magnesia mixture should be added, and $\frac{1}{3}$ vol. of alcohol, or the precipitation will be incomplete. Bäckström has proposed (Abstr., 1893, ii, 299) to separate the sulphuric acid from the arsenic acid in the oxidised precipitate by simply heating until the former is expelled, but the authors show that however carefully the heat is applied, a loss of arsenic acid occurs before all the sulphuric acid is driven off.

Arsenious acid, intended for precipitation as sulphide, is best dissolved in potassium hydrogen carbonate, as its solution in an alkali hydroxide oxidises gradually to arsenate on exposure to air. Before precipitating, it must be acidified with a quarter to one-half its volume of hydrochloric acid of 1.12 sp. gr.; passing hydrogen sulphide for half an hour suffices for complete precipitation, but one hour is recommended. Subsequent expulsion of the dissolved hydrogen sulphide, either by warming or by carbonic anhydride, is neither necessary nor desirable, and since arsenious sulphide is not soluble in hydrogen sulphide water, moreover, the passage of carbonic anhydride does not diminish the excess of sulphur in the precipitate if filtration is commenced within 10 minutes of stopping the current of hydrogen sulphide, but, on the other hand, dissolves traces of arsenic from the precipitate, in consequence of the reaction $\text{As}_2\text{S}_3 + 3\text{H}_2\text{O} = \text{As}_2\text{O}_3 + 3\text{H}_2\text{S}$. One and a-half hours drying at $105-110^\circ$ suffices to give a constant weight; in an atmosphere of carbonic anhydride, no loss of weight takes place at 140° . M. J. S.

Boric acid. By A. VILLIERS and M. FAYOLLE (*J. Pharm.*, 1895, [6], 2, 241—244).—The ordinary tests for boric acid leave much to be desired. Those founded on the turmeric reaction are unsatisfactory, because the colour change is not sufficiently characteristic. Those based on the flame coloration, on the one hand, if applied directly to the solid substance, are liable to give misleading indications if copper be present, as is often the case in wine ash, and to be masked by the more intense colorations due to sodium, &c.; and, on the other hand, if applied to the alcoholic distillate, they are open to the objection that the delicacy of the test is very variable, the intensity of the coloration depending on the stage of the distillation at which it is observed, as well as on the amount of boric acid present.

In testing for boric acid in wines, the authors recommend the repeated distillation of the ash (from 25 c.c.) with small quantities of methylic alcohol (3 c.c., three times), after moistening it with concentrated sulphuric acid (1 c.c.). The whole of the boric acid passes over, and its amount may be estimated colorimetrically with fair accuracy, by comparison of the flame with those given by standard solutions of the acid. Quantities from 0.5 to 0.1 milligram may be detected in this way.

A number of natural wines which were examined by this process

did not contain a trace of boric acid. The marked quantities found by other authors must, therefore, either be attributed to the presence of copper, or to the introduction of boric acid in fining the wines.
JN. W.

Estimation of Boric acid. By HENRI JAY and DUPASQUIER (*Compt. rend.*, 1895, **121**, 260—262).—In order to estimate boric acid by converting it into methylic borate, the substance is very slightly acidified with hydrochloric or sulphuric acid, mixed with 25 to 30 c.c. of methylic alcohol, and placed in a flask, which is connected with another flask containing a normal alkali hydroxide solution free from carbonates, and also with a condenser, in such a way that the methylic borate formed in the first flask passes through the alkali solution in the second flask, whilst the methylic alcohol, which is again set free, is condensed, and falls back into the first flask. After boiling for about an hour and a half, the alkali solution is heated to expel methylic alcohol, very slightly acidified with dilute hydrochloric acid, again heated to expel carbonic anhydride, and titrated with decinormal alkali until neutral to litmus paper. Two drops of an aqueous solution of the blue C.4.B. are added, and the addition of alkali is continued until the first colour-change begins. The second quantity of alkali, less 0.2 to 0.3 c.c., according to the volume of the liquid, gives the quantity of boric acid present. In order to obtain accurate results, the temperature and volume of the liquid operated on must be constant, and methylic alcohol and carbonic anhydride must be expelled.

Pure wines contain from 0.0105 to 0.022 gram of boric anhydride per litre; cider and perry 0.011 to 0.017; urine, 0.008 to 0.017. The acid was not found in the bone or flesh of an ox. The accuracy of the estimation is slightly affected by the presence of fluorides, but not by that of other salts.
C. H. B.

Estimation of Carbonic Oxide in Air. By JOHN S. HALDANE (*J. Physiol.*, 1895, **18**, 463—469).—The method described depends on the fact that when a hæmoglobin solution is shaken with air containing carbonic oxide, the proportion of the pigment which finally combines with the gas varies with the percentage of carbonic oxide in the air. This proportion is determined by a colorimetric method, standard carmine solution being added to a standard solution of diluted blood till it becomes as pink as that which has been shaken with the air containing the poisonous gas. The details of the method, which yields delicate rather than accurate results, are described in full.
W. D. H.

Gold and Silver in Copper and Copper Matte. By ERNEST A. SMITH (*Chem. News*, 1895, **72**, 76—77).—Commenting on the discrepancies that often occur in the results obtained by different assayers working on the same sample, it is suggested that neglect to take notice of the silver in the test-lead, use of one acid only, and that probably strong, for parting, and bad balances are the most frequent causes of the differences alluded to.
D. A. L.

Detection and Estimation of Mercury in Urine. By ADOLF JOLLES (*Monatsh.*, 1895, **16**, 684—692).—From 100 to 300 c.c. of urine, according to the amount of mercury supposed to be present, is treated with stannous chloride and free hydrochloric acid in presence of about 2 grams of granular gold. The precipitated mercury amalgamates with the gold, which is afterwards washed by decantation and treated with hot concentrated nitric acid, whereby the mercury is dissolved. The solution thus obtained is diluted with water, and, on the addition of stannous chloride, yields a precipitate even when only a minute trace of mercury is present.

To determine the mercury quantitatively, the amalgam of gold obtained as above is washed with water, alcohol, and ether, weighed in a hard glass tube, and the mercury distilled off. The loss in weight gives directly the amount of mercury present.

G. T. M.

Volumetric Estimation of Platinochlorides; Estimation of Potassium, Ammonium, Nitrogen, and Platinum. By LUCIEN L. DE KONINCK (*Chem. Zeit.*, 1895, **19**, 901—902).—The platinochlorides of potassium or ammonium obtained during an analysis, may, instead of being weighed, be volumetrically treated by applying the reduction principle of Correnwinder and Contamina. The precipitate is dissolved in boiling water and heated for some time with calcium formate, which soon removes the platinum, leaving potassium or ammonium and calcium chlorides, also free hydrochloric acid in solution.

The mixture is neutralised by means of calcium carbonate suspended in water, and, after filtering, the chlorine is estimated as usual by means of silver nitrate. Six atoms of chlorine represent 2 atoms of potassium, ammonium, or nitrogen, and 1 atom of platinum. The calcium carbonate is made from calcium nitrate and sodium carbonate.

L. DE K.

Quantitative Separation of Benzene from Light Petroleum. By ROBERT HENRIQUES (*Chem. Zeit.*, 1895, **18**, 958—959).—5—7 c.c. of the mixture is introduced into a 25-c.c. glass stoppered cylinder, divided to 0.2 c.c., and shaken with twice its volume of sulphuric acid containing 5 per cent. of added sulphuric anhydride, until nothing more is dissolved.

The benzenes soon become sulphonated and dissolve, whilst the light petroleum is scarcely attacked, and floats on the surface of the acid; its volume may then be read off.

L. DE K.

Analysis of the Cyanide Solutions used in the Extraction of Gold. By GEORGE A. GOYDER (*Chem. News*, 1895, **72**, 80—82).—See this vol., ii, 28).

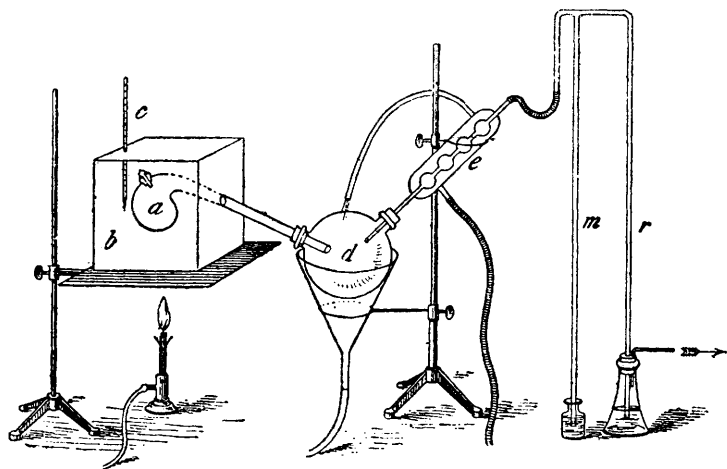
Estimation of Glycerol in Fermented Liquors. By J. LABORDE (*J. Pharm.*, 1895, [6], **1**, 568—570).—The liquor (50 c.c.) is boiled nearly to dryness (1 c.c.) in a flask containing a quantity of lead shot (100 grams). The glycerol, which is retained in combination with the acid of the wine, is liberated from the residue by the addition of finely powdered, slaked lime, with which it is incorporated

into a stiff paste by agitation with the shot. If sugar is present, the lime is previously moistened with alcohol, and a larger quantity is used. The liberated glycerol is extracted from the paste by repeatedly shaking with alcohol-ether, and the extract having been acidified with sulphuric acid (10—15 drops), the solvent is as far as possible distilled off, and the residual alcohol removed by repeatedly boiling with water; the acid aqueous solution thus obtained is evaporated to dryness and carbonised, and the amount of glycerol calculated from that of the carbon obtained.

Trial analyses of wine and beer, to which various amounts of glycerol were added, are stated to have been satisfactory.

The ratio of alcohol to glycerol in red wines appears to vary within the limits 1 : 10 and 1 : 16. JN. W.

Estimation of Glycerol in Wine and Beer. By ALFRED PARTHEIL (*Arch. Pharm.*, 1895, **233**, 391—398).—The liquid under examination (50 c.c.) is mixed with calcium carbonate and concentrated to 10—15 c.c.; it is then filtered into a tubulated retort, *a*, of 100 c.c. capacity, fitted at the tubulus with a bored cork, which is closed with a glass rod; the retort is heated in an air bath, *b*, the bottom being of sheet iron, the sides and top of asbestos paper, fastened by means of water-glass. The bath is heated at 120°, and when the contents of the retort have been distilled almost to dryness, the bath is cooled to 60°, the apparatus exhausted, and the distillation continued at 180° (25—30 mm.); this requires 1·5 hours. The apparatus is allowed to cool, the pressure restored, water (10 c.c.) added to the retort, and the distillation repeated at 120°. All the glycerol will be



found in the receiver, *d*; should it be coloured, it must be distilled again under similar conditions. The glycerol is determined by Baumert and Schaumann's method (*Abstr.*, 1892, 1529). The contents of the receiver and condenser, *e*, are washed into an Erlenmeyer

flask, diluted to about 200 c.c., sodium hydroxide (8—10 grams) added, and then potassium permanganate solution (5 per cent.), until the liquid remains bluish-black; it is next heated on the water bath for an hour, decolorised by means of sulphurous anhydride, acidified with glacial acetic acid (20 c.c.), and evaporated until free from sulphurous anhydride. The residue is diluted to about 200 c.c., and calcium chloride added in excess, the mixed precipitate of calcium oxalate and calcium sulphate being collected on an asbestos filter, and washed until the liquid ceases to affect potassium permanganate solution; it is then dissolved in dilute sulphuric acid, and the oxalic acid estimated in the usual manner by means of standard potassium permanganate solution (about 5:1000). Under the above conditions, 1 mol. glycerol yields 1 mol. oxalic acid, and the analyses given of wine, beer, and aqueous glycerol solutions agree closely with the theoretical.

In the sketch, *m* is the manometer, and *r* a tube and valve to prevent the back flow of water from the pump. If the pressure in the apparatus is reduced without previously cooling, in the manner described by von Törring, loss of glycerol always occurs.

J. B. T.

Estimation of Pentoses and Pentosans in Diffusion Cuttings, Sugar Beet, and some Food Stuffs. By A. STIFT (*Chem. Centr.*, 1895, i, 448—449; from *Österr.-ung. Zeit. Zucker-Ind.*, **23**, 925—933).—The substance under examination (2·5—5·0 grams), together with hydrochloric acid, sp. gr. = 1·06 (100 c.c.), is placed in a flask (300 c.c. capacity), which is fitted with a funnel and heated by means of a bath of fusible metal; after distilling during 10—12 minutes, when 30 c.c. should have passed over, hydrochloric acid (30 c.c.) is added, the distillation continued, and these operations repeated until the production of furfuraldehyde ceases. The distillate is treated exactly in the manner described by Tollens. The whole analysis requires 5½—6 hours; it presents no special difficulties, and affords valuable information as to the relative worth of the most varied food stuffs.

J. B. T.

Relative Proportion of Glucose and Levulose in Sweet Wines. By F. JOSEF KÖNIG (*Chem. Zeit.*, 1895, **19**, 999—1000).—The relative proportion of glucose and levulose in sweet wines may be calculated from the copper-reducing power, coupled with a polarimetric observation. The colouring and tannin matters are best removed by means of basic lead acetate, as the use of animal charcoal causes a slight loss of sugar.

If there is a large excess of levulose present, it may be concluded that the wine has been prepared by fermenting a concentrated juice, and then suddenly stopping the fermentation by adding alcohol or by other means; whilst, if the dextrose is largely in excess, its wilful addition may be suspected. If both are present in about equal amounts, with perhaps a slight excess of levulose, no particular conclusion can be drawn; the relation of the dextrose to the levulose will not decide the question whether the grape-juice has, from the commencement, been fortified with cane or starch sugar. On the

whole the analysis of sweet wines is still in a somewhat unsatisfactory condition.

L. DE K.

Estimation of Glycogen in Liver and Muscle. By WLADIMIR A. KISTIAKOFFSKY (*Chem. Centr.*, 1895, i, 449; from *Pharm. Zeit. Russ.*, 34, 25).—The use of 0.1—0.3 per cent. solutions of alkali instead of 2 per cent., for the extraction of glycogen, is recommended by Brücke; but glycogen may also be obtained by extracting the finely divided substance 5—6 times with boiling water, and pressing the residue. In addition to the glycogen, the liquid contains alkali albuminates, gluten, and traces of peptone; these are removed by precipitation with potassiummercuric iodide after the liquid has been concentrated and acidified with hydrochloric acid; the glycogen is precipitated from the filtrate by means of alcohol (compare Huizinga, this vol., i, 6).

J. B. T.

Estimation of Glycogen. Detection of Albumoses in Presence of Glycogen. By D. HUIZINGA (*Pflüger's Archiv*, 1895, 61, 32—38).—See this vol., i, 6.

Estimation of Formic acid. By FRANZ FREYER (*Chem. Zeit.*, 1895, 19, 1184—1185).—The author's process has been invented for the purpose of estimating calcium formate in the presence of acetate. The mixture having been distilled with dilute sulphuric acid in a current of steam until the distillate is no longer acid, the total acidity is estimated in an aliquot part of the distillate by means of standard soda, and another portion of the liquid is neutralised with aqueous soda and concentrated to a small bulk. It is then boiled with a mixture of dilute sulphuric acid and potassium dichromate, which is without any action on the acetic acid, but rapidly and completely oxidises the formic acid to carbonic anhydride and water. The strength of the dichromate must, of course, be accurately known, and the excess is afterwards determined as usual by means of potassium iodide and sodium thiosulphate. To better see the change in colour, a little metaphosphoric acid may be added.

L. DE K.

The Resorcinol Test for Tartaric acid. By GEORGES DENIGÈS (*J. Pharm.*, 1895, [6], 1, 586—589; compare Mohler, *Abstr.*, 1891, 867).—Mohler's test, which consists in the addition of the substance to be tested to a dilute solution of resorcinol in concentrated sulphuric acid at 120°, with the consequent production, if a tartrate is present, of a violet coloration, is open to the objections that the reagent is perishable, that the test is applicable only to solid substances, thus necessitating the evaporation of solutions to dryness, and that the violet coloration, or one closely resembling it, is produced by various oxidising agents. The author has modified the process in a manner to obviate these defects.

A solution of pure, white resorcinol (2 grams) in very dilute sulphuric acid ($\frac{1}{2}$ c.c. to 100 c.c. water) is quite stable, and, by adding a portion of this to about 20 vols. of concentrated acid at the time of testing (2 or 3 drops to 2 c.c.), a solution is obtained equivalent to Mohler's reagent. A small quantity of the liquid to be tested (1 or 2 drops) is added to the reagent, and the mixture gradually

warmed to 115° — 140° , when, if tartaric acid is present, the characteristic violet-red colour is developed. It is due to the presence of a broad absorption band in the spectrum, extending from $\lambda = 510$ to $\lambda = 545$, and best seen with solutions diluted with concentrated sulphuric or acetic acids.

If the coloration appears before heating, it is due to the presence of an oxidising agent in the liquid, and this must be previously removed by reduction with copper-zinc and dilute sulphuric acid (5 c.c. of solution to be tested, 5–6 drops copper sulphate solution, 2 grams of zinc, and 1 c.c. of acid). Tartaric acid can in this way be detected in a few drops of a 1 per cent. solution containing, in addition, 10 per cent. each of sodium nitrite, and potassium nitrate, chromate, and chlorate.

Substances such as cane sugar, which are blackened by sulphuric acid, are best eliminated by Mohler's method of precipitating the acid as lead salt, and washing the latter with dilute nitric acid before decomposing it and making the test.

JN. W.

Analysis of Fish Oils. By VIKTOR VEDRÖDI (*Chem. Zeit.*, 1895, 19, 600–601).—The author calls attention to the enormous difference in composition of various commercial brands of fish oil, particularly as regards their acidity and percentage of unsaponifiable matter. The acidity was found to vary from 0.74 to 38.9 per cent., and the unsaponifiable matter from 0.6 to 82 per cent.

No sample should be used for tanning purposes unless the acidity and the unsaponifiable matter do not exceed 15 and 4 per cent. respectively.

L. DE K.

Examination of Fats by Means of the Refractometer. By HEINRICH BECKURTS and H. HEILER (*Arch. Pharm.*, 1895, 233, 423–428).—The objects of this investigation were the determination (1) of the influence of temperature on the refractive power of various fats and oils, and (2) the relationship, if any, between the refractive power, the percentage of volatile acids, and the iodine additive capacity; the experiments were conducted with a Zeiss' refractometer. The increase in the refractive power in scale divisions, for a rise of 1° , is as follows:—Butter = 0.54–0.58; olive oil = 0.6; cotton seed oil = 0.5–0.6; ground nut oil = 0.6–0.7; oil of apricots = 0.4–0.6; sun-flower seed oil = 0.5–0.6; sesame oil = 0.6–0.7; almond oil = 0.5–0.6; oil of peaches = 0.6. No relationship was observed between the refractive power of butter and of deer fat and their iodine absorption value, but high refractive power is accompanied by a relatively great additive power for iodine in the case of the above oils, and also in the following: poppy oil, cocoa nut oil, palm oil, butter (?), tallow, lard, margarine. Nothing is said directly of the volatile fatty acids.

J. B. T.

Deer Fat. By HEINRICH BECKURTS and F. OELZE (*Arch. Pharm.*, 1895, 233, 429–430).—Deer fat melts at 49 – 49.5° and solidifies at 48° , the corresponding values for tallow and beef fat are 44 – 45.5° and 32 – 36° , and 43 – 44.5° and 37° respectively. The fatty acids of

deer fat melt at 49.5° , of tallow at $45-47^{\circ}$ of beef fat at $44.5-46^{\circ}$; the iodine absorption values are $19.8-21$, $32.7-46.2$, and $35.4-44$ respectively. The refractive powers (Zeiss' refractometer) at 40° are 44.5 , 46 , and 45 . J. B. T.

Lard Analysis. By A. GOSKE (*Chem. Zeit.*, 1895, **19**, 1043—1045).—The author recommends crystallising the sample from ether at a temperature of $12-13^{\circ}$. With a little practice, it will be found comparatively easy to distinguish microscopically between tallow-stearin and any lard-stearin which, however, does not readily crystallise.

When applying the silver test, the author uses the original Bechi test as approved by the Italian Committee. The test gains in delicacy if the lard is first pressed at a temperature of $26-30^{\circ}$, and the reaction applied to the expressed oil. L. DE K.

Examination of Pepper. By WALTER BUSSE (*Zeit. anal. Chem.*, 1895, **34**, 638—643; from *Arbeiten K. Gesundheitsamte*, **9**, 509).—The methods of estimating moisture, ash, sand, and total alcoholic extract are described. The estimation of the colouring matters, which occur only in the husk, is considered important; these are extracted from the residue insoluble in alcohol by digesting it with hot sodium hydroxide solution, and are precipitated by lead acetate from the extract after acidifying with acetic acid. The amount of lead so precipitated is called the "lead number," and seldom exceeds 0.122 gram per gram of pepper. M. J. S.

Nutmeg. By WALTER BUSSE (*Zeit. anal. Chem.*, 1895, **34**, 643—644; from *Arbeiten K. Gesundheitsamte*, **11**, 390).—The total ash should not exceed 5 per cent., nor the amount insoluble in hydrochloric acid (sand) 0.5 per cent. For estimating the fat, 2 grams of the grated powder is extracted with ether for eight hours, then dried, rubbed down with quartz sand, and again extracted for four hours; after evaporating the ether, the fat is absorbed by 8 grams of ignited sand, and dried at 100° for five hours only, to avoid oxidation. The amount varies from 30 to 40 per cent. M. J. S.

Margarine Cheese and its Analysis. By M. KÜHN (*Exper. Stat. Record*, 1895, **7**, 158; from *Molk. Zeit.*, 1895, **9**, 185—187).—The percentage composition of the cheese is said to be valueless in distinguishing it from natural cheese. The following determinations are recommended to be made in the ether extract; sp. gr. at 100° by means of a Westphal balance and König's butter areometer; insoluble fatty acids (Hehner's method); volatile fatty acids (Reichert-Meißl-Wollny) Köttesdorfer saponification equivalent; angle of refraction in the Zeiss-Wollny butter refractometer. A number of results obtained with different cheeses are given in the original paper. N. H. J. M.

Composition of Meat Extract. By F. JOSEF KÖNIG and A. BÖMER (*Zeit. anal. Chem.*, 1895, **34**, 548—562).—It has hitherto

been accepted that meat extracts contain gelatin and other proteïds. Thus, C. Karmrodt found 10·4 per cent. of gelatin in Liebig's extract, Kemmerich (Abstr., 1894, ii, 150) 33·23 per cent. of proteïds, and Stutzer (Abstr., 1893, 146) 20·5 to 22·6 per cent. of peptone. The numbers obtained by Kemmerich were deduced from the results of fractional precipitation by alcohol, on the assumption that gelatin is precipitated by 60 per cent. alcohol, albumoses by 80 per cent., and peptones only by 90 per cent. The authors have repeated Kemmerich's work, but employing Kjeldahl's process, instead of weighing the precipitates, as was done by Kemmerich (a method to which they take exception), have obtained numbers for gelatin and albumoses which are less than one-third of Kemmerich's. In Liebig's extract, the mode of manufacture would seem to exclude the possibility of more than traces of gelatin being present. The usual mode of estimating peptone, namely, precipitation by phosphomolybdic acid, is erroneous, since this reagent gradually (in the course of 5—7 days) throws down the flesh bases also, about 90 per cent. of the total nitrogen being precipitable. The absence of peptone may be shown qualitatively, as after precipitating with ammonium sulphate to ensure the absence of albumoses, the filtrate does not give the biuret reaction. In the cases of Kemmerich's meat peptone, and Cibils' meat extract obtained by means of the digestive ferment of *Carica Papaya*, the filtrate is pale enough for the detection of traces. The filtrates from Liebig's and Kemmerich's meat extracts are darker, but the colour is incompetent to mask the reaction if as much as 2—3 per cent. of peptone is present (see, however, Stutzer, *loc. cit.*). Stutzer's statement as to the presence of ammonia is confirmed, but no evidence could be obtained of the presence of amido- or acid amido-compounds. Albumose (precipitable by ammonium sulphate or zinc sulphate; see next abstract) is the only proteïd present in notable quantity, but the flesh bases constitute by far the largest portion of the total nitrogenous constituents.

M. J. S.

Precipitation of Albumoses by Zinc Sulphate. By A. BÖMER (*Zeit. anal. Chem.*, 1895, **34**, 562—567).—Zinc sulphate possesses many advantages over ammonium sulphate for the separation of albumose from peptone. The precipitation is equally complete, comparative estimations by means of the two reagents having given identical numbers in the four meat extracts examined by the author and J. König (preceding abstract), whilst the filtrates in all cases gave no indication of the presence of a proteïd by the biuret reaction. The presence of zinc sulphate in no way disturbs the Kjeldahl process, so that the nitrogen in the precipitate can be estimated without the need of applying any correction. The filtrate is at once suitable for precipitation by phosphomolybdic acid, either for the purpose of testing the completeness of the washing or (after strongly acidifying with an equal volume of dilute sulphuric acid, 1 : 4) for the estimation of peptone, flesh bases, &c. Since phosphates give a precipitate with zinc sulphate, it is desirable to slightly acidify the solution with sulphuric acid; 1 c.c. of acid (1 : 4) is

therefore to be added to 50 c.c. of solution containing 1—2 grams of the extract, and previously freed from insoluble and coagulable substances; the liquid is then saturated in the cold with a small excess of finely powdered zinc sulphate, and the precipitate washed with a cold saturated solution of the same salt. Although meat extracts contain ammonia, and ammonia forms with zinc sulphate a sparingly soluble double salt, in no case was ammonia found in the albumose precipitate, but, on the contrary, the whole of the ammonia of the original substance was obtained when the filtrate from the zinc precipitate was distilled with sufficient magnesia to precipitate all the zinc present and leave the liquid strongly alkaline. M. J. S.

Estimation of Gelatin in Meat Extracts and Commercial Peptones. By ALBERT STUTZER (*Zeit. anal. Chem.*, 1895, **34**, 568—570).—The following is the exact method of carrying out the estimation of which the outline was previously given (*Abstr.*, 1895, ii, 543). Sand, previously ignited and freed from fine dust by a sieve, is used instead of asbestos for absorbing the solution in the tinfoil capsule. After complete drying at 100°, the contents of the capsule are powdered, and, with the cut up capsule, placed in a beaker, where they are extracted four times with absolute alcohol, filtering the extracts through an asbestos filter, but leaving as far as possible the insoluble matter in the beaker. The beaker (marked *a*) together with four others (*b*, *c*, *d*, *e*) are then plunged into crushed ice, as also a flask containing a mixture of 100 c.c. of alcohol, 300 grams of ice, and cold water to 1 kilogram. Of this mixture, the temperature of which must not exceed 5°, about 100 c.c. is poured on the sand, stirred therewith for two minutes, and decanted into beaker *b*; the second decantate is poured into *c*, and so on, until the last washing is colourless, a fragment of ice being added to each as soon as it is poured off. Three funnels are then arranged with filter beds of long-fibred asbestos supported by perforated porcelain plates, and connected with a pump by which gentle and gradually increasing suction can be applied. The contents of beaker *a* are filtered through the first, finally transferring the sand to the funnel, *b* is poured into the second, and *c* and *d* into the third. The three filters, as well as that through which the absolute alcohol extract had been filtered, are then thoroughly washed with the ice cold dilute alcohol, transferred to a basin, and repeatedly extracted by boiling with water. The aqueous extract, after filtration, is concentrated and submitted to Kjeldahl's process for the estimation of the gelatin. In the process given in *Abstr.*, 1893, 146, the albumose (line 2 from bottom of page) must be corrected for any coagulable albumin present in the meat extract.

M. J. S.

General and Physical Chemistry.

Dissociation of Optically Active Salts in Solution. By PHILIPPE A. GUYE and B. ROSSI (*Bull. Soc. Chim.*, 1895, [3], 13, 464—469).—It is well known that the specific rotatory powers of the salts of optically active monobasic acids, at sufficiently low concentrations, are identical with those of the acids themselves, whilst those calculated from the rotatory powers of more concentrated solutions are usually divergent. Although this is accounted for in a general manner by the theory of electrolytic dissociation, the optically active acids being, as a rule, comparatively little dissociated, and having approximately normal cryoscopic constants and electrolytic conductivities at temperatures at which their salts are almost completely dissociated; yet a complete examination of an individual case has not hitherto been made. The authors have, therefore, determined the rotatory powers of various inorganic and organic salts of active valeric acid, a substance which was chosen on account of the comparative simplicity of its constitution due to the absence of alcoholic hydroxyl.

The specific rotatory power of the aqueous solution of the acid is $[\alpha]_D = +17.3^\circ$, whilst that of the pure acid is $+13.64^\circ$; but this difference may be due as much to molecular association as to electrolytic dissociation.

The specific rotatory powers of the lithium, sodium, potassium, and rubidium salts at concentrations corresponding with 2.46 grams of the acid in 100 c.c., and calculated on the amounts of the salts actually present, are respectively $[\alpha]_D = +8.0^\circ$, $+7.2^\circ$, $+6.4^\circ$, and $+5.4^\circ$; whilst those calculated on the amounts of acid present, on the supposition that the salts are completely dissociated into their ions, are respectively $+8.5^\circ$, $+8.8^\circ$, $+8.9^\circ$, and $+10.1^\circ$. The approximate identity of the rotatory powers of the salts of metals differing so widely in atomic weight, is noteworthy, considering the great difference between those of the alkylic valerates; the lithium, potassium, and rubidium salts are the most dissociated, the mean rotatory power of the three being approximately half that of the acid at the same concentration.

As might be expected from theory, the specific rotatory powers of aqueous solutions of valeric acid are diminished alike by dilution and by rise of temperature. The rotatory power, $[\alpha]_D = +12.02^\circ$, of an acid somewhat less active than that used in the foregoing determinations, became $+14.6^\circ$ in an aqueous solution containing 3.732 grams per litre, but was diminished to $+14.4^\circ$, when the concentration was reduced to 1.239 gram per litre, and was reduced in the two cases to $+14.36^\circ$ and $+14.2^\circ$, when the temperature was raised from 18° to 25° .

The rotatory powers of aniline, pyridine, and diethylamine valerates in aqueous solutions of the same concentration of acid as those of the alkali salts, and calculated on the amounts of the salts actually present, are $[\alpha]_D = +6.30^\circ$, $+6.36^\circ$, and $+4.99^\circ$ respectively, whilst

those calculated on the amounts present on the hypothesis of complete dissociation are $+12.4^\circ$, $+11.26^\circ$, and $+8.77^\circ$. These results are in harmony with the cryoscopic constants of the bases. The specific rotatory powers of alcoholic solutions of the foregoing salts and of those of dimethylaniline, quinoline, and phenylhydrazine containing the same amounts of acid as before, are practically identical with that of an alcoholic solution of the acid of the same concentration, except in the case of the diethylamine salt, the activity of which is some 50 per cent. less. With this exception, therefore, these salts are completely dissociated in alcoholic solution, a conclusion similar to that arrived at by Ghira from a study of the cryoscopic properties of benzene solutions of the corresponding acetates.

It is thus useless to determine the optical activity of solutions of the organic salts of optically active substances in organic solvents; and where organic solvents are used, investigation must, in future, be limited to inorganic salts. JN. W.

Colour Change of Dilute Solutions of Potassium Chromoxalate. By FRIEDRICH HAMBURGER (*Ann. Phys. Chem.*, 1895, [2], 56, 173—174).—A dilute solution of potassium chromoxalate, $K_3Cr(C_2O_4)_3$, when placed in a cylindrical vessel was found to exhibit in general a green colour by transmitted daylight, but showed purple streaks at the edges and in the centre. By artificial light, the solution appeared only purple. An examination of the absorption spectrum was therefore made, and showed a wide absorption band between the wavelengths 630 and 530, and complete absorption at the wave-length 470. Hence the yellow, orange, blue, and violet rays are absorbed from the spectrum, only red and indigo remaining; the colour resulting from these two is dependent on the proportion in which they are present in the incident light rays. H. C.

Emission of Light by Organic Substances in the Gaseous, Liquid, and Solid Condition. By EILHARD WIEDEMANN and G. C. SCHMIDT (*Ann. Phys. Chem.*, 1895, [2], 56, 18—26).—The authors find by numerous experiments that many organic compounds exhibit fluorescence in the gaseous condition; this fluorescence is blue or violet with retene, phenanthrene, anthracene, anthraquinone, chrysene, indigo, and naphthalene, and a magnificent reddish-brown with naphthazarin. The absorption spectra of solutions of the hydrocarbons in this list, all lie in the extreme violet or ultra-violet, and, therefore, as in the case of benzene and toluene, the absorption of the gaseous hydrocarbons probably lies still further towards the ultra-violet end of the spectrum. Anthraquinone also absorbs violet rays, and naphthazarin, in alcoholic solution, green, blue, and violet rays. The emission spectra lie, therefore, in accordance with Stokes' rule, nearer the less refrangible end of the spectrum than the absorption spectra, and the spectra of organic vapours are fluorescence spectra in the usual sense of the term.

Many organic compounds in the gaseous state yield characteristic spectra under the influence of electrical discharges, but the spectra obtained in this way do not correspond with the absorption spectra. In

the liquid state many organic compounds become luminous under the influence of the cathode discharge, and the colour in this case is the same as that of the vapour. Solid organic compounds also frequently exhibit cathode-luminosity, but the colour is not in all cases identical with that of the liquid.

H. C.

Measurement of High Temperatures. By L. HOLBORN and W. WIEN (*Ann. Phys. Chem.*, 1895, [2], 56, 360—396).—The Le Chatelier thermo-couple of platinum and a platinum-rhodium alloy containing 10 per cent. of rhodium, has been compared by the authors with the air thermometer up to the temperature 1450°. This instrument gives very constant readings if protected from the possible action of carbon. Its use in high temperature measurements is, therefore, to be preferred to that of employing the change of resistance of a platinum wire, for with the latter, even if between each measurement the temperature coefficient between 0° and 100° is redetermined, this affords no guarantee for the behaviour at high temperatures. The authors find, also, that Callendar's formula for the change of resistance with change of temperature is not sufficiently exact to admit of a far reaching extrapolation. A comparison with the air thermometer can be most readily effected with the thermo-couple, as it can be directly introduced into the air vessel, and must in this way acquire the same temperature as that of the expanding air. The following melting points were measured :—

Silver.....	971°	Nickel.....	1484°
Gold	1072	Palladium.....	1587
Copper.....	1082	Platinum	1780

H. C.

Some Melting and Boiling Points. By HENRI LE CHATELIER (*Compt. rend.*, 1895, 121, 323—326).—Experiments made with a thermoelectric couple protected by a thin film of glass and graduated up to the boiling point of zinc (930°) give 1050° to 1060° as the melting point of gold. Experiments made with another couple, taking the melting point of silver as 954°, show that the melting point of gold is 1055—1060°. The author concludes that the melting point of gold as given by Violle, 1045°, is too low, but that the error is certainly not more than 20°, that none of the more recent estimations of this melting point are sufficiently accurate to warrant their substitution for Violle's number, and that it is very desirable to retain the scale of high temperatures at present actually in use until new and more exact experiments made by direct comparison with the air thermometer shall give the true melting point of gold to within a very few degrees (compare Heycock and Neville, *Trans.*, 1895, 1024).

C. H. B.

Explosion of Endothermic Gases. By LÉON MAQUENNE (*Compt. rend.*, 1895, 121, 424—427).—When a small quantity of mercuric fulminate is exploded in contact with nitrous oxide, the latter is decomposed with a violent explosion. Acetylene under similar conditions only begins to decompose, about 95 per cent. of the gas remaining unaltered, and the explosive wave is not propagated through the mass of the gas. With a larger quantity of fulminate

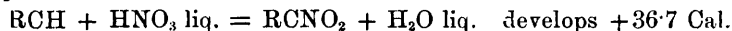
(about 1 gram) the acetylene is decomposed, and the explosive wave travels through a distance which depends on the diameter of the tubes and the conditions under which the explosion takes place.

C. H. B.

Nitro-substitutions. By CAMILLE MATIGNON and DELIGNY (*Compt. rend.*, 1895, 121, 422—424).—

	Heat of combustion.		Difference from parent compound.
	Const. volume.	Const. pressure.	
Orthonitrophenol	688·6	688·2	44·3
Paranitrophenol	689·5	689·1	43·4
Orthonitrobenzoic acid .	731·1	730·4	44·0
Metanitrobenzoic acid ..	727·7	727·0	47·4
Paranitrobenzoic acid ..	729·6	728·8	45·5
Paranitroacetanilide....	969·2	968·9	47·9
Nitrobenzaldehyde.....	801·2	800·3	41·4

The third column gives the difference between the heats of combustion, at constant pressure, of the nitro-derivative and the parent substance. The position-isomerides have practically the same heats of combustion. With the exception of nitrobenzaldehyde, the difference is practically constant and is about 45, whatever the function of the compound in which substitution takes place. The equation deduced from this difference is



the thermal disturbance being indential with that found by Berthelot in the case of the hydrocarbons benzene, toluene, naphthalene, &c.

C. H. B.

Combination of Mercuric Cyanide with Bromides. By RAOUL VARET (*Compt. rend.*, 1895, 121, 398—400).—In the following table, column I, gives the heat of dissolution of the salt, column II the heat developed by the interaction of solutions of mercuric cyanide and the particular bromide, and column III the heat of formation of the solid salt from its proximate constituents, the salts being regarded as solid and the water as liquid.

	I.	II.	III.
2Hg(CN) ₂ , 2NaBr, 4H ₂ O...	−24·14 Cal.	+0·98 Cal.	+18·52 Cal.
2Hg(CN) ₂ , 2NH ₄ Br, 2H ₂ O..	−20·97 „	+1·06 „	+ 7·23 „
2Hg(CN) ₂ , 2LiBr, 7H ₂ O ...	−18·31 „	+1·25 „	+36·26 „
2Hg(CN) ₂ , BaBr ₂ , 7H ₂ O ...	−20·98 „	+1·29 „	+20·27 „
2Hg(CN) ₂ , SrBr ₂ , 6H ₂ O ...	−18·60 „	+1·24 „	+29·84 „
2Hg(CN) ₂ , CaBr ₂ , 7H ₂ O ...	−19·82 „	+1·25 „	+40·47 „
2Hg(CN) ₂ , MgBr ₂ , 8H ₂ O...	−15·97 „	+1·44 „	+54·71 „
2Hg(CN) ₂ , ZnBr ₂ , 8H ₂ O...	−20·82 „	+1·33 „	+31·15 „
Hg(CN) ₂ , CdBr ₂ , 3H ₂ O	−12·5 „	+0·66 „	+10·5 „

At the ordinary temperature, the solutions are slightly alkaline to litmus, and slowly give the isopurpurate reaction with a picrate of the same base as is combined with the bromine. It follows that whilst almost all the mercury is in combination with cyanogen, a

small quantity is in combination with the bromine. The proportion of the latter increases as the temperature rises. These results are in accord with the thermochemical data. C. H. B.

Distillations with an Automatic Mercury Pump. By FRIEDRICH KRAFFT and W. A. DYES (*Ber.*, 1895, **28**, 2583—2589).—The paper contains a description of an air pump devised some 16 years ago by v. Babo. It consists of a Sprengel mercury pump which works in the vacuum of a water suction-pump and so need not be more than 30—40 cm. long; the mercury, which falls down the short Sprengel tube, is carried up again to the top of the apparatus by a current of air drawn in by the water-pump, and the apparatus is thus automatic and continuous in its action. It is comparatively small in size, so that it can be placed, by means of clamps and a retort-stand, on the laboratory bench, and it does not require more than 600—650 grams of mercury; a vacuum of less than 1 mm. is attainable by its means.

By means of this pump the boiling- or sublimation-points of several substances were determined. Mannitol boils at 276—280° under about 1 mm., at 285° under 2.5 mm., and at 290—295° under 3—3.5 mm. pressure. Dulcitol boils at 275—280°, 287—288°, and 290—295° under the same pressures. α -Hydroxybutyric acid boils at 84° under 1.5 mm. pressure. Succinic acid sublimates at 156—157° under 2.2 mm., at 160—165° under 2.5—3 mm. pressure; fumaric acid at 165° under 1.7 mm., mesaconic acid at 139—141° under 1.5 mm., at 143—145° under 2 mm., and itaconic acid at 140—141° under 1.5 mm. pressure; maleic and citraconic acids do not sublime without forming some anhydride. Wood's metal was used to heat the distillation flasks; the temperature of the bath need not be more than a few degrees above the boiling-point of the liquid, but if the substance does not boil, but sublimes, a much greater difference of temperature, 40—60° above the sublimation point, was found to be necessary.

C. F. B.

Density Determinations of Extremely Dilute Solutions. By FRIEDRICH KOHLRAUSCH (*Ann. Phys. Chem.*, 1895, [2], **56**, 185—200).—The author has further improved the method of determining the density of very dilute solutions, which he had formerly employed in conjunction with Hallwachs (*Abstr.*, 1894, ii, 441). The size of the ball of glass used was greatly increased, the suspension from the balance being effected by means of a thin platinum wire which was first coated electrolytically with platinum and afterwards ignited. The rough surface thus produced, satisfactorily removes the difficulties and irregularities observed when a smooth wire is employed. As very slight variations of temperature exercise a very disturbing influence on the results, owing to the unequal expansion of the solution and of the glass ball, it was necessary to confine the observations within limits of temperature between which this influence is at a minimum, the limits within which a variation of a few thousandths of a degree may be allowed, being from 4° to 8°. A limiting error of 10^{-7} has thus been reached in the determinations.

Observations were made with solutions of cane sugar, magnesium

sulphate, acetic acid, and sulphuric acid. On the assumption that the water undergoes no contraction in volume, the molecular volumes ϕ of the dissolved substances are calculated by means of the formula

$$\phi = A - 1000 \frac{s - 1}{m},$$

where A is the weight of the equivalent, m the number of gram-equivalents per litre in the solution, and s is the density. The results are given in the following table, and for the purpose of comparison, the results formerly obtained with Hallwachs at the higher temperature of 18° are included.

m .	Sugar. $A = 341 \cdot 1$.		Magnesium sulphate. $A = 60 \cdot 23$.		Acetic acid. $A = 60 \cdot 00$.		Sulphuric acid. $A = 49 \cdot 04$.	
	$6 \cdot 0^\circ$.	18° .	$6 \cdot 3^\circ$.	18° .	$5 \cdot 5^\circ$.	18° .	$6 \cdot 0^\circ$.	18° .
0.0002	207.0	—	-4.5	—	(51.3)	—	(6.1)	—
0.0006	207.3	—	-4.5	—	(50.0)	—	(5.5)	—
0.001	207.32	209.0	-4.6	—	(49.8)	—	(5.5)	—
0.002	207.41	209.0	-4.6	-3.4	49.61	—	5.9	6.9
0.005	207.48	209.5	-4.14	-3.21	49.69	50.7	6.92	7.94
0.01	207.56	209.59	-3.91	-2.65	49.72	50.88	7.71	9.32
0.03	207.70	209.71	-3.37	-2.15	49.85	51.0	9.75	11.80
0.05	207.8	209.77	-3.03	-1.74	49.88	51.04	10.75	12.77
0.1	208.0	209.89	-2.45	-1.21	49.93	51.10	12.03	14.05
1	209.9	211.5	+0.9	+1.68	50.21	51.34	15.54	16.96
5	—	215.9	+6.0	+6.58	51.05	52.14	17.57	18.52

It will be seen that the continual increase in the molecular volumes with rising concentration is to be observed in these as in the former determinations. The only exceptions occur in very dilute solutions of acetic and sulphuric acids; here a complicated behaviour or disturbance occurs similar to that noticed in conductivity determinations, the molecular contraction increasing only up to a certain degree of dilution, and then decreasing. It is probable that the explanation of this peculiarity may be found in the traces of impurities present in the water used, as these undoubtedly affect the density determinations in these extremely dilute solutions in a marked manner. The molecular volumes are throughout one to two units greater at 18° than at 6° .
H. C.

Influence of Hydrochloric acid and Chlorides on the Photochemical Decomposition of Chlorine Water. By EUTHYME KLIMENKO (*Ber.*, 1895, **28**, 2558—2564).—Normal solutions of hydrochloric acid and of various chlorides were diluted with equal volumes of chlorine water and exposed in sealed tubes to sunlight, together with some tubes containing chlorine water only. When the chlorine in the latter had completely disappeared, the other tubes were

opened, and the amount of chlorine still remaining in them was estimated. It was found that the hydrochloric acid had most retarded the disappearance of the chlorine, very little chlorine having disappeared in this case; if the amount left in the hydrochloric acid tube be taken as 1, then the amounts left in the tubes containing the chlorides are represented by the following numbers: LiCl 0.308, NaCl 0.173, KCl 0.090, MgCl_2 0.550, CaCl_2 0.390, SrCl_2 0.302, BaCl_2 0.285, ZnCl_2 0.200, CdCl_2 0.042. The different metals group themselves in the same order as in the periodic system.

The action of chlorine on water is said to result in the formation, first of hydrochloric and hypochlorous, and finally of hydrochloric and chloric, acids. The retarding action of hydrochloric acid is ascribed to its reconverting the hypochlorous acid formed into chlorine. It is further suggested that metallic chlorides are partly converted into chlorates by the chloric acid formed, and that the hydrochloric acid thus liberated reacts with hypochlorous acid to reform chlorine, owing to which circumstance the metallic chlorides retard the disappearance of the chlorine.

C. F. B.

Heating Apparatus for Drying Ovens. By JOHANNES THIELE (*Ber.*, 1895, **28**, 2601—2602).—The tubes which carry the rows of small jets used in heating drying ovens are usually clamped to the legs of the stand by means of screws; these screws become so hot that it is generally impossible to touch them, and consequently difficult to regulate the temperature of the oven. The author has devised a stand, figured in the paper, in which the tube of jets is carried by a rail that slides up and down between two of the legs, and is pressed against these by a spring, so that it is held fixed in any position. To alter the position, it is merely necessary to press two handles together; these act as levers, and release the pressure of the spring; they are, moreover, fairly long and have wooden ends, so that they do not get too hot to touch.

C. F. B.

A Modified Condenser. By J. J. L. VAN RIJN (*Ber.*, 1895, **28**, 2388).—The modification consists in bending the inner tube so that the whole condenser can be rotated, without being removed from the vessel to which it is attached, in such a manner that it can be used either as an ordinary condenser or a reflux condenser.

It appears from the drawing which is appended, that the modified condenser could not be used in connection with any vessel with a narrow aperture.

A. H.

Modification of Liebig's Condenser. By HUGO MICHAELIS (*Ber.*, 1895, **28**, 2615).—The author brought forward the modification recently described by van Rijn (preceding abstract) about 10 years ago (*Chem. Zeit.*, 1886, 1556).

A. H.

Inorganic Chemistry.

Decomposition of Hydrogen Peroxide. By WALTHER SPRING (*Zeit. anorg. Chem.*, 1895, **10**, 161—176).—When a 38 per cent. solution of hydrogen peroxide is heated at 60° in a platinum dish which has been previously polished, no decomposition takes place; at a higher temperature small bubbles of gas are formed. When, however, the inside of the dish is scratched with a needle, small gas bubbles are formed at the scratch, even at the ordinary temperature, and on raising the temperature a brisk evolution of gas takes place. A 70 per cent. solution of hydrogen peroxide contained in a glass flask is only slowly decomposed when a current of air from a wide tube is passed through it; if, however, a capillary tube is used, brisk decomposition takes place.

The author has examined the decomposition of hydrogen peroxide when mixed with various solutions. Five c.c. of a 36 per cent. hydrogen peroxide solution is mixed with 5 grams of each solution, and allowed to remain for a given time at 65° in a thermostat, and the remaining hydrogen peroxide titrated in acid solution with permanganate; the solutions employed contain 1 gram mol. of dry salt to 38.5 gram mols. of water. Hydrochloric and nitric acids decompose the peroxide quickly, but sulphuric and phosphoric acids have a preservative action. The decomposing action of salt solutions is more energetic the feebler the base they contain and the more readily the acid they contain is oxidised or reduced by hydrogen peroxide; thus, lithium and sodium sulphates produce only a slight decomposition, magnesium chloride about double, and aluminium chloride about treble this decomposition, whilst sodium and potassium carbonates entirely decompose hydrogen peroxide. This decomposition is due to the acid function which hydrogen peroxide evinces towards some salts. If a solution of hydrogen peroxide is gradually added to a solution of an alkali carbonate, pure oxygen is evolved; if, however, the carbonate is added to an excess of hydrogen peroxide, it is completely converted into alkali dioxide and carbonic anhydride. The ratio of the concentration of two solutions of a salt is not equal to the ratio of their decomposing action on hydrogen peroxide.

E. C. R.

Action of Hydrogen Peroxide on Ammoniacal Copper Compounds: Preparation of Oxygen. By DIOSCORIDE VITALI (*L'Orosi*, 1895, 1—5).—When hydrogen peroxide is added to ammoniacal copper sulphate, a brisk effervescence takes place in the cold, and oxygen is evolved in abundance, the copper salt remaining unchanged; and as an indefinite amount of the peroxide can be decomposed by means of the same portion of the metallic compound, pure oxygen may be very conveniently prepared by allowing the ordinary aqueous peroxide (3—4 per cent.) to flow steadily from a tap-funnel into a saturated solution of ammoniacal copper sulphate

(20—30 c.c.) contained in a fairly capacious Woulff's bottle. The gas is dried and purified from ammonia by means of sulphuric acid.

The mechanism of the action appears to be analogous to that of the decomposition of potassium chlorate in presence of manganese dioxide; the cupric compound reacts with the peroxide, yielding a cuprous salt and free oxygen, and the cuprous compound is then re-oxidised by another portion of the peroxide.

The same action occurs to a limited extent with copper hydroxide alone, and to a varying extent with ammoniacal solutions of other metallic salts, but in no case is it continuous as with copper; mercuric oxide and mercurous nitrate, for instance, are visibly reduced, and the action ceases as soon as the reduction is complete.

The method is not applicable to the estimation of hydrogen peroxide in aqueous solution, as the whole of the oxygen is not evolved, part being employed in oxidising ammonia to nitrous and nitric acids, which may be detected in the solution at the end of the operation.

JN. W.

Formation of Ozone. By OTTO BRUNCK (*Zeit. anorg. Chem.*, 1895, 10, 222—247; see also *Abstr.*, 1893, ii, 454).—The author has already proved that the intense odour of the oxygen prepared from a mixture of potassium chlorate and manganese dioxide is chiefly due to the presence of ozone. A further examination of the gas shows that only a very minute trace of chlorine is evolved, equal in amount to that evolved in the decomposition of pure potassium chlorate alone. The gas examined was evolved at a temperature of 320°. If the mixture is heated at 400° and above, at which temperature the dioxide commences to decompose, then more chlorine is evolved.

It has already been shown that oxygen is ozonised when passed over heated manganese dioxide or certain other metallic oxides, and this action has been further examined. The ozone is estimated as follows: the gas is passed through a neutral solution of potassium iodide, which is then acidified with dilute sulphuric acid, and titrated with N/100 sodium thiosulphate solution. The action of ozone on an acidified potassium iodide solution takes place according to the equation $O_3 + 2KI = 2I + K_2O + O_2$; when, however, ozonised oxygen is passed through a neutral solution of potassium iodide, the action takes place according to the equations $O_3 + 2KI = 2I + K_2O + O_2$ and $6I + 3K_2O = KIO_3 + 5KI$. The second reaction does not take place quantitatively, and there remains free iodine and potassium hydroxide in the solution; the latter is partially converted by the ozone into potassium dioxide, so that finally the solution contains potassium iodate, potassium hydroxide, and potassium dioxide. Hydrogen peroxide is not formed. When the solution is acidified, a third part of the iodine, equivalent to the ozone, is liberated at once, whilst the reaction with the hydrogen peroxide liberated from the potassium dioxide is only complete after 1—2 hours.

Manganese dioxide when heated in a current of carbonic anhydride at 400°, and to an incipient red heat, does not yield ozone. In a current of oxygen at 400°, 6·5 grams of the dioxide gave in one hour 9·57 milligrams of ozone; at an incipient red heat, it gave 7·46 milli-

grams. The formation of ozone from a mixture of potassium chlorate and manganese dioxide increases with the amount of manganese dioxide; manganous oxide acts in a similar way to the dioxide, but much less ozone is formed.

Cobalt oxide, Co_2O_3 , behaves in a similar way to manganese dioxide, but in the presence of nascent oxygen the amount of ozone formed is greater in proportion to the amount of cobalt oxide employed. The compound $\text{K}_2\text{Co}_9\text{O}_{16}$, prepared by fusing cobalt carbonate with potassium hydroxide, when heated at 200° gives off three atoms of oxygen, but no ozone is formed.

Nickel oxide behaves in a similar way to the above; apparently, it is not altered by heating in oxygen, and after heating some time still evolves chlorine when treated with hydrochloric acid, and ozone when again heated in oxygen. The reaction with potassium chlorate takes place violently at 300° , and less ozone is formed than in the case of cobalt.

Silver oxide, when heated in a current of carbonic anhydride at 250° , gives only a slight trace of ozone, which is probably due to the action of the oxygen formed on undecomposed oxide; in a current of oxygen at 280° , it forms ozone. Silver peroxide was prepared by the electrolysis of silver nitrate; 1.22 gram heated at 300° gave 7.68 milligrams of ozone. Only a very small quantity of oxygen is evolved from a mixture of silver oxide and potassium chlorate at 360° ; above 400° , the chlorate decomposes slowly without the formation of ozone.

Mercuric oxide when heated at 400° does not give off ozone, but when heated in a current of oxygen, a small quantity of ozone is formed; probably the greater part of the ozone is destroyed by the metallic mercury. With potassium chlorate, it behaves in a similar way to silver oxide.

Lead peroxide yields ozone when heated either in a current of carbonic anhydride or of oxygen, but with potassium chlorate at 320 – 350° , only a very small quantity of ozone is formed, and the peroxide is reduced to red lead and litharge. When heated to redness in a current of oxygen, red lead and litharge yield small quantities of ozone.

Chromic anhydride (3.39 grams), when heated at 260 – 280° , yields ozone (1.52 milligram). Chromium oxide heated at 400° in a current of oxygen, yields small quantities of ozone.

Uranium trioxide does not yield ozone in an atmosphere of carbonic anhydride; in oxygen, small quantities of ozone are formed. When heated with potassium chlorate, it yields potassium uranate and chlorine. The hydrate of the tetroxide, when heated at 150° in a current of carbonic anhydride, yields water and oxygen, but no ozone is formed, as probably hydroxyl groups are eliminated, which decompose into water and oxygen.

The author was unable to detect the formation of ozone from platinum oxide, as the compound always contains chlorine, which is evolved on heating. Gold oxide was prepared by precipitation of gold chloride with potassium hydroxide; the mixture is acidified with sulphuric acid, and the precipitate dissolved in nitric acid,

reprecipitated by dilution with water, and dried at 150° ; 1.44 grams of the oxide heated in a current of carbonic anhydride at $230-280^{\circ}$ gave 21 milligrams of ozone, and 1.85 grams heated in oxygen gave 34.4 milligrams of ozone.

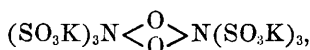
E. C. R.

The so-called Oxysulphazotic acid or Nitrosodisulphonic acid. By ARTHUR R. HANTZSCH and WILLIAM SEMPLE (*Ber.*, 1895, 28, 2744—2751).—Potassium nitrosodisulphonate, $\text{ON}(\text{SO}_3\text{K})_2$, prepared by the oxidation of potassium hydroxylaminedisulphonate by means of lead peroxide, has, according to Raschig, the formula

$(\text{SO}_3\text{K})_2\text{N} \begin{smallmatrix} \diagup \text{O} \diagdown \\ \diagdown \text{O} \diagup \end{smallmatrix} \text{N}(\text{SO}_3\text{K})_2$; to this the authors make the following

objections: (1) The group $\text{N} \begin{smallmatrix} \diagup \text{O} \diagdown \\ \diagdown \text{O} \diagup \end{smallmatrix} \text{N}$: has never previously been observed, and its chromophoric character has not been proved; (2) the acidic character of two linked pentavalent nitrogen atoms is unique; (3) the difficulty of explaining the change of colour from orange-yellow to deep violet-blue which takes place when the salt is dissolved; (4) when reduced, no hydrazine derivatives are formed. The authors regard the compound as a derivative of nitric peroxide with the simple formula $\text{ON}(\text{SO}_3\text{K})_2$, the oxidation of nitrous acid to nitric peroxide, and of potassium hydroxylaminedisulphonate to potassium nitrosodisulphonate being analogous, the relationship between the yellow solid salt and the blue solution is similar to that between colourless solid N_2O_4 and coloured NO_2 . Cryoscopic molecular weight determinations failed to give satisfactory results on account of the instability of the compound. If the oxidation of the hydroxylamine derivative is incomplete, blue crystals are formed; these are also obtained by mixing solutions, saturated at 40° , of potassium hydroxylaminedisulphonate (3.5—4 parts) and potassium nitrosodisulphonate (1 part), and consist of solid solutions containing 1—4 per cent. of the latter in the former. The colour of the crystals varies, according to the composition, from ultramarine to sky blue, they are comparatively stable, and the content of nitrosodisulphonate may be determined by means of potassium iodide and acetic acid, titrating the liberated iodine with potassium thiosulphate.

Raschig's potassium nitrosotrisulphonate,



formed by the action of water on potassium nitrosodisulphonate, is also regarded as monomolecular $\text{ON}(\text{SO}_3\text{K})_3$; cryoscopic molecular weight determinations were unsatisfactory, and the electrolytic conductivity of its solution does not follow Ostwald's rule, but it is similar to "dibenzsulphhydroxamic acid," $\text{ON}(\text{SO}_2\text{Ph})_3$, the molecular weight of which agrees with the formula. Raschig's objection to the simpler formula for potassium nitrosotrisulphonate was based on its non-formation by the oxidation of potassium azotrisulphonate,

$\text{N}(\text{SO}_3\text{K})_3$; but this has little weight since tertiary ammonium derivatives do not yield amine oxides, ONR_3 , when oxidised.

J. B. T.

Dinitrososulphonic acid (Nitroxysulphurous acid). By ARTHUR R. HANTZSCH (*Ber.*, 1895, **28**, 2751—2754).—The author replies to Divers and Haga's criticisms (*Trans.*, 1895, 452) of his previous paper on this subject (*Abstr.*, 1895, ii, 75). Their statement that he believes in the existence of two potassium nitroxysulphites is based on a misapprehension, as reference to his paper shows, and he takes exception to their formula $\text{OK}\cdot\text{N}\cdot\text{NO}\cdot\text{SO}_3\text{K}$ on the following grounds: (1) The salt, being similar to nitrosylsulphuric acid, $\text{O}\cdot\text{N}\cdot\text{O}\cdot\text{SO}_3\text{H}$, should be readily hydrolysed to sulphuric acid and hyponitrous acid; actually it is, in alkaline solution, very stable. (2) Until decomposed it does not give the reactions of the sulphates as might be expected. (3) Their general remarks on acids and bases are in conflict with the theory of dissociation. (4) The fact that alkyl hydrogen sulphates are not directly precipitated by barium chloride is explained by the fact that all alkyl derivatives are non-electrolytes. The above objections do not apply to the author's formula $\text{O} < \begin{smallmatrix} \text{N}\cdot\text{OK} \\ \text{N}\cdot\text{SO}_3\text{K} \end{smallmatrix}$ with which Raschig's $\text{ON}\cdot\text{N}(\text{OK})\cdot\text{SO}_3\text{K}$ may be tautomeric (compare Divers and Haga, *Trans.*, 1895, 1098).

J. B. T.

Formation of Hydrogen Selenide. By H. 'PÉLABON (*Compt. rend.*, 1895, **121**, 401—404; compare *Abstr.*, 1894, ii, 135 and 447).—In order to avoid any error that may arise from the fact that when selenium is heated in a mixture of hydrogen and hydrogen selenide, it absorbs a certain quantity of the latter, which is partially liberated on cooling, the author has determined by Ditte's method the composition of the gas obtained by heating hydrogen at various temperatures in presence of the smallest possible excess of selenium. The relation p_1/p_2 of the partial pressure of the hydrogen to that of the hydrogen selenide was determined for each temperature, and the results are expressed with great accuracy by the equation of Gibbs and Duhem, $\log(p_1/p_2) = M/T + N \log T + Z$, in which M, N, and Z are constants, T is the absolute temperature of the experiment, and the logs are Napierian logs. Experiments at 350°, 440°, and 510° give 13170.3, 15.53, and 119.88 respectively for the values of M, N, and Z. It follows from the equation that the ratio $r = p_2/p_1 + p_2$ should have a maximum value at the temperature t when $t = M/N - 273$. With the values already given for M and N, $t = 575^\circ$, and this deduction is confirmed by experiment. It also follows from Duhem's equations and the values found for M and N that the heat of formation of hydrogen selenide should be -17380 minor calories, whereas Fabre's experiments gave the value -18000.

C. H. B.

Tellurium. By LUDWIG STAUDENMAIER (*Zeit. anorg. Chem.*, 1895, **10**, 189—221).—Telluric acid is most easily obtained by dissolving tellurium in an excess of dilute nitric acid and then adding a slight excess of chromic acid. The solution is evaporated to crystallisation and

the crystals washed with nitric acid and dissolved in a small quantity of water. The solution is treated with a few drops of alcohol to reduce any chromic acid remaining, and precipitated by the addition of nitric acid. Finally, the product is dissolved in water and evaporated to dryness on the water bath. Telluric acid separates from water at the ordinary temperature in crystals, with $2\text{H}_2\text{O}$, belonging to the irregular system; these are stable in the air, and are not hygroscopic. When precipitated from its aqueous solution with nitric acid, regular crystals resembling lead nitrate are obtained, together with the ordinary modification; these also contain $2\text{H}_2\text{O}$. From solutions at 0° , it crystallises with $6\text{H}_2\text{O}$ in large, tetragonal crystals resembling monopotassium phosphate; these crystals effloresce at the warmth of the hand, and are converted into the ordinary modification. When dried over phosphoric acid, they do not decompose even in a vacuum.

Pure tellurium compounds are obtained from the crude Hungarian tellurium as follows. The finely powdered substance is dissolved in dilute nitric acid, the solution evaporated with strong hydrochloric acid, and filtered; the tellurium is then precipitated from the filtrate with sulphurous acid, and after being washed with hydrochloric acid and water, it is dissolved in nitric acid, oxidised with chromic acid, and the telluric acid treated as described above.

The atomic weight of tellurium was determined in accordance with the following equations $\text{H}_2\text{TeO}_4, 2\text{H}_2\text{O} = \text{TeO}_2 + \text{O} + 3\text{H}_2\text{O}$ or $\text{Te} + 3\text{O} + 3\text{H}_2\text{O}$ and $\text{TeO}_2 = \text{Te} + \text{O}_2$. The first decomposition is brought about by heating in a glass flask. The reduction in the second and third decomposition is performed as follows. The telluric acid or dioxide is mixed with finely divided silver and pure silica, and the mixture contained in a platinum or porcelain boat, covered with a layer of finely divided silver. The admixture with silver prevents the slightest trace of tellurium from volatilising. The mixture is first heated in a glass tube until the telluric acid is dehydrated, then in a current of hydrogen, while the temperature is gradually raised from 250° to 400° , and finally for a short time at a dull red heat. The results of all the experiments (number of experiments not stated) agree closely with 127.6 ($\text{O} = 16$) for the atomic weight of tellurium.

Experiments on the fractional crystallisation of telluric acid are described, which show that all fractions give the same atomic weight. The author discusses at length the work of Brauner (*Trans.*, 1889, 382; 1895, 549) and of Retgers (*Zeit. physikal. Chem.*, 1893, 12, 596).

E. C. R.

A Hydrate of Arsenic Trisulphide and its Decomposition by Pressure. By WALTHER SPRING (*Zeit. anorg. Chem.*, 1895, 10, 185—188).—The hydrate, $\text{As}_2\text{S}_3 + 6\text{H}_2\text{O}$, is obtained by precipitating a solution of arsenic trichloride containing hydrochloric acid with hydrogen sulphide, and drying the precipitate in a current of air having a relative humidity of 70 per cent. at the ordinary temperature. It has a somewhat lighter yellow colour than ordinary arsenic trisulphide, and easily loses its water when warmed. The sp. gr. = 1.8806 at 25.6° , and the specific volume = 53.174; whereas the

specific volume of the sum of its constituents As_2S_3 and $6\text{H}_2\text{O}$ is 50.626, therefore, according to the author's theory, it must decompose when submitted to pressure. It is, in fact, decomposed quantitatively into water and anhydrous trisulphide when submitted to a pressure of 6000—7000 atmospheres. If the density of ice is taken for the calculation of the specific volume of the hydrate, the number 52.662 is obtained, which shows that the water is present in the solid form.

E. C. R.

The Compounds of Arsenic with Selenium and of Arsenic, Selenium, and Sulphur. By EMERICH SZARVASY (*Ber.*, 1895, **28**, 2654—2661; compare Clever and Muthmann, this vol., ii, 18).—*Arsenic pentaselenide*, As_2Se_5 , was prepared by heating the two constituents in the requisite proportion in sealed tubes filled with nitrogen; it forms a black, lustrous, brittle mass, and may be purified by fractional distillation under diminished pressure. It is not readily acted on by the ordinary solvents, but fuming nitric acid oxidises it to selenious and arsenic acids. Alkaline hydroxides and hydrosulphides readily dissolve it, but the resulting yellow solutions decompose when exposed to the air, and, when acidified with the mineral acids, yield the pentaselenide in the form of a reddish-brown, flocculent precipitate. Vapour density determinations made at 750 — 800° show that the molecule of As_2Se_5 has undergone decomposition, probably into As_2Se_3 and Se_2 ; at still higher temperatures (1050 — 1100°) the vapour density shows that the molecule of As_2Se_5 has split up into three simpler molecules.

Sodium monoselenoarsenate, $\text{Na}_3\text{AsO}_3\text{Se} + 12\text{H}_2\text{O}$, is one of the compounds formed on dissolving arsenic pentaselenide in sodium hydroxide, but as the solution readily decomposes when exposed to the air, it is necessary to work in an atmosphere of hydrogen. The salt may be obtained as colourless crystals on the addition of methylic alcohol to the aqueous solution; the crystals, when left exposed to the air, lose their water of crystallisation and turn red, owing to the liberation of selenium.

Sodium selenoarsenate, $\text{Na}_3\text{AsSe}_4 + 9\text{H}_2\text{O}$, obtained together with the preceding compound when arsenic pentaselenide is dissolved in sodium hydroxide, crystallises in ruby-red needles, which rapidly lose their water of crystallisation when exposed to the air; it is readily soluble in water, and the solution readily undergoes decomposition, selenium being deposited. Mineral acids throw down the pentaselenide from its alkaline solutions in the form of a reddish-brown flocculent precipitate.

Arsenic triselenobisulphide, $\text{As}_2\text{Se}_3\text{S}_2$, is obtained when arsenic bisulphide and selenium are heated together in the requisite proportions in an atmosphere of nitrogen; it is best purified by repeated distillation under low pressure, and then forms a black, highly glistening substance which, in thin plates, has a purple-red colour. In chemical properties it resembles arsenic pentaselenide; it is soluble in alkalis, and is precipitated unaltered on the addition of an acid. Vapour densities taken at 550 — 600° indicated that dissociation had taken place.

Arsenic diselenotersulphide, $\text{As}_2\text{Se}_2\text{S}_3$, may be obtained in a similar manner from arsenic tersulphide and selenium. It differs from the

preceding compound in being ruby-red in thin plates. The vapour density at 750° indicates that dissociation has taken place.

J. J. S.

Atomic Weight of Helium. By N. A. LANGLET (*Zeit. anorg. Chem.*, 1895, **10**, 289—292).—The helium was prepared as follows. A hard glass tube, 1 metre long, is filled first with a column (10 cm. long) of manganese carbonate, then with a mixture of powdered cleveite (3 parts) and potassium pyrosulphate (2 parts), and then with a column (10 cm. long) of copper oxide. The air is expelled from the tube by carbonic anhydride, the copper oxide heated to redness, and the tube then heated, as in the case of an organic analysis. The gas produced is collected over 50 per cent. potassium hydroxide, and finally passed through a tube containing layers of copper oxide, phosphoric anhydride, and magnesium powder, the copper oxide and magnesium being heated to redness. The gas so prepared, when examined spectroscopically in a Giessler's tube, was found to be free from nitrogen, hydrogen, and argon. The density was determined by weighing 100 c.c. in a glass balloon, and was found to be 0.139 (air = 1) or 2.00 ($H = 1$). The velocity of sound in the gas was then determined, and from this the ratio of the specific heats at constant pressure and at constant volume. The ratio obtained = 1.67, whence the molecule of helium contains only one atom, and the atomic weight = 4.

E. C. R.

Combination of Magnesium with Argon and with Helium.

By LOUIS J. TROOST and LÉON V. R. OUVRARD (*Compt. rend.*, 1895, **121**, 394—395).—It is not indispensable to pass a mixture of argon and helium with nitrogen over red-hot magnesium or lithium before introducing it into the spectrum tubes. The tubes are furnished with magnesium wires, and a Ruhmkorf coil is used which has a Marcel-Deprez contact breaker. The dry gas is introduced, and a powerful current is passed. At first the nitrogen is slowly absorbed, but when the pressure is reduced to a certain point, the magnesium wires become very hot, and the nitrogen combines with the metal very rapidly. The nitrogen spectrum disappears, and that of helium or argon, or both, becomes visible.

If a powerful discharge is continued for some time, the argon and helium disappear, seemingly because they combine with the vapour of the magnesium. Platinum under similar conditions seems likewise to volatilise and combine with argon.

C. H. B.

Argon, a New Constituent of the Atmosphere. By LORD RAYLEIGH and WILLIAM RAMSAY (*Phil. Trans.*, 1895, **186**, 187—241).—It has been shown by Rayleigh that nitrogen extracted from chemical compounds is about $\frac{1}{2}$ per cent. lighter than "atmospheric nitrogen" (*Abstr.*, 1895, ii, 444), the chemically prepared nitrogen previously used having been obtained from nitric oxide, from nitrous oxide, and from ammonium nitrite by the use of hot iron. As it appeared desirable to show that the agreement of numbers obtained for chemical nitrogen does not depend on the use of a red heat in the process of purification, experiments were tried with nitrogen liberated from

carbamide by the action of sodium hypobromite, which gas it was hoped would require no further purification than drying. But the gas so obtained was obviously contaminated, attacked vigorously the mercury of the Töpler pump, and was described as smelling like a dead rat. Its weight proved to be in excess even of the weight of atmospheric nitrogen, and it was only after passing the gas over hot metals that the corrosion of the mercury and the evil smell were in great degree obviated, and the weight was found to correspond with that of the chemical nitrogen previously examined. Nitrogen can, however, be prepared from ammonium nitrite without the employment of hot tubes, which, in spite of a slight nitrous smell, shows no appreciable difference in density from that prepared by treatment with hot metals.

To the above list may be added nitrogen, prepared in yet another manner, whose weight was determined subsequently to the isolation of the new dense constituent of the atmosphere; in this case the nitrogen was actually extracted from air by means of magnesium. The nitrogen thus separated was then converted into ammonia by the action of water on the magnesium nitride, and afterwards liberated in the free state by means of calcium hypochlorite. The purification was conducted in the usual way, and included in one case passage over red-hot copper and copper oxide, but this was subsequently omitted. With or without exposure to red-hot copper, the "chemical" nitrogen derived from "atmospheric" nitrogen possesses the usual density.

Experiments were also made to prove that the ammonia produced from the magnesium nitride is identical with ordinary ammonia, and contains no other compound of a basic character. For this purpose, the ammonia was converted into ammonium chloride and the percentage of chlorine determined by titration with a solution of silver nitrate, which had been standardised with pure sublimed ammonium chloride. It was found that ammonium chloride prepared from magnesium nitride obtained by passing atmospheric nitrogen over red-hot magnesium contains practically the same percentage of chlorine as pure ammonium chloride. It may be concluded, therefore, that red-hot magnesium withdraws from atmospheric nitrogen no substance other than nitrogen capable of forming a basic compound with hydrogen.

That the discrepancy between the weights of chemical and atmospheric nitrogen cannot be due to the presence of known impurities has already been proved (*loc. cit.*). It was thought that the lightness of the gas extracted from chemical compounds might be explained by partial dissociation of nitrogen molecules N_2 into detached atoms. But as the silent electric discharge has no effect on the density of either kind of gas, and as the density of a sample of chemically prepared nitrogen showed no sign of increase after storage of the gas for eight months, this view had to be abandoned. Regarding it as established that one or other of the gases must be a mixture, the simplest assumption, in view of the above facts, was to admit the existence of a second ingredient in air, from which oxygen, moisture, and carbonic anhydride had already been removed. If the density of the supposed gas were double that of nitrogen, $\frac{1}{2}$ per cent. only by

volume would be needed, or, if the density were but half as much again as that of nitrogen, then 1 per cent. would still suffice.

The positive evidence in favour of the prevalent doctrine that the inert residue from air after withdrawal of oxygen, water, and carbonic anhydride is all of one kind appears to be derived from the experiments of Cavendish (*Phil. Trans.*, 1785, **75**, 372). By sparking a mixture of air and oxygen in the presence of alkali for the absorption of the acid product of the reaction, and subsequent removal of the excess of oxygen by a solution of liver of sulphur, Cavendish found that only a small bubble of air remained unabsorbed, "which certainly was not more than 1/120th of the bulk of the " nitrogen " let up into the tube," and therefore concluded "that if there is any part of the " nitrogen " of our atmosphere which differs from the rest, and cannot be reduced to nitrous acid, we may safely conclude that it is not more than 1/120th part of the whole." Cavendish was satisfied with this result, and does not decide whether the small residue was genuine, but the experiments hereafter described render it not improbable that his residue was really of a different kind from the main bulk of the nitrogen, and contained the gas now called argon.

With a view of isolating, if possible, the unknown and overlooked constituent, or, it might be, constituents, the existence of which in atmospheric nitrogen had thus been rendered probable, this gas was submitted to examination.

The earliest attempts to isolate the suspected gas were made by the method of Cavendish, using a Ruhmkorff coil of medium size actuated by a battery of five Grove cells. When the mixed gases were in the right proportion, a rate of absorption of about 30 c.c. per hour could be attained. In a particular instance, starting with 50 c.c. of air and gradually adding oxygen, the volume was at length reduced to 1 c.c. On treatment with alkaline pyrogallol, the gas shrank to 0.32 c.c. That this small residue could not be nitrogen was argued from the fact that it had withstood the prolonged action of the spark, although mixed with oxygen in nearly the most favourable proportion. To this residue another 50 c.c. of air was added, and the whole worked up with oxygen as before. The residue was now 2.2 c.c., and after removal of oxygen 0.76 c.c. In another case, a mixture of 5 c.c. of air with 7 c.c. of oxygen was sparked for one hour and a quarter, the residue was 0.47 c.c., and, after removal of oxygen, 0.06 c.c. Several repetitions giving similar results, it became clear that the final residue did not depend on anything that might happen when sparks passed through a greatly reduced volume, *but was in proportion to the amount of air operated on.*

Difficulty was experienced in accumulating a sufficient quantity for examination of the residue which refused to be oxidised, owing, as was proved later on, to the solubility of the gas in water. At length, however, a sufficiency was collected to allow of sparking in a specially constructed tube, when a comparison with the air spectrum, taken under similar conditions, proved that, at any rate, the gas was not nitrogen.

Since nitrogen, at a bright red heat, is easily absorbed by magnesium, best in the form of turnings, an attempt was successfully

made to remove that gas from the residue left after eliminating oxygen from air by means of red-hot copper. In a preliminary experiment, in which a quantity of atmospheric nitrogen was admitted into contact with red-hot magnesium, pumped off, and then treated again with fresh magnesium, the original volume of 1094 c.c. was reduced to 50 c.c., which resisted rapid absorption. It still contained nitrogen, however, judging by the diminution of volume which it experienced when allowed to remain in contact with red-hot magnesium. Its density was, nevertheless, determined by weighing a small bulb of about 40 c.c. capacity, first with air and afterwards with the gas. The density found was 14.88, and the gas, therefore, was heavier than air.

An arrangement was then adopted by means of which a quantity of atmospheric nitrogen could be brought repeatedly into contact with fresh quantities of magnesium heated to redness. About 10 litres of gas were taken and treated in this manner, until the volume was reduced to 200 c.c. Unfortunately some of the nitrogen was lost by leakage, so that exact measurements could not be taken. The density of this residual gas was found to be 16.10, but as it appeared advisable to continue the absorption of nitrogen, it was again treated with fresh magnesium. The volume was thus reduced to a little over 100 c.c., and the density was now found to be 19.086 ($O = 16$). A portion of the gas was then mixed with oxygen, and submitted to a rapid discharge of sparks for four hours in presence of caustic potash. It contracted, and on absorbing the excess of oxygen with alkaline pyrogallol, the contraction amounted to 15.4 per cent. of the original volume. If the gas contained 15.4 per cent. of nitrogen of density 14.014, and 84.6 per cent. of other gas, the density of the mixture being 19.086, calculation leads to the number 20.0 for the density of this other gas.

A vacuum-tube was filled with a specimen of the gas of density 19.086, and it could not be doubted that it contained nitrogen, the bands of which were distinctly visible. It was probable, therefore, that the density of the pure gas lay not far from 20 times that of hydrogen. At the same time many lines were seen which could not be recognised as belonging to the spectrum of any known substance.

If atmospheric nitrogen contains two gases of different density, it should be possible to obtain direct evidence of the fact by the method of atmolysis, and experiments were made with this object. The atmolyser was prepared by combining a number of churchwarden tobacco pipes; eight pipes connected in simple series, and placed in a large glass tube, closed in such a way that a partial vacuum could be maintained in the space outside the pipes by a water-pump, giving the best results thus obtained. One end of the combination of pipes was connected with the interior of an open bottle containing sticks of caustic alkali, the object being mainly to dry the air. The other end of the combination was connected to a bottle aspirator, initially full of water, and so arranged as to draw about 2 per cent. of the air which entered the far end of the pipes. The air thus obtained was treated exactly as ordinary air had been treated in determinations of the density of atmospheric nitrogen. The density of the gas from the

above prepared air was in every case greater than that from unprepared air, and to an extent much beyond the possible errors of experiment. The conclusion seems inevitable that "atmospheric nitrogen" is a mixture and not a simple body.

To complete the verification, negative experiments were made to prove that argon is not derived from nitrogen or from chemical sources. In one case 3 litres, and in another case about $5\frac{1}{2}$ litres of chemical nitrogen, prepared from ammonium nitrite, were treated with oxygen in precisely the manner in which atmospheric nitrogen had been found to yield argon. The final residue was in neither case more than 3.5 c.c., and this consisted mainly of argon, the source of which is to be found in the water used for the manipulation of the large quantities of gas employed. If atmospheric nitrogen had been used, the final residue should have been about 10 times the above amount. A similar set of experiments was carried out with magnesium, and led to the same conclusion.

A description is given of the methods adopted for the separation of argon on a large scale, both by the oxygen and the magnesium process. In the latter case, a quantitative experiment was carried out on a large scale, the amount of argon from 100 litres of "atmospheric" nitrogen, measured at 20° , being collected after treatment with magnesium, and measured at 12° . An accident led to the loss of about 4 litres of nitrogen during the process, and the total residue, after absorption of the nitrogen, being 921 c.c., the yield is therefore 0.986 per cent. It may be concluded, with probability, if allowance be made for the solubility of the argon in the water over which it was collected, that argon forms approximately 1 per cent. of the atmospheric nitrogen. This result is confirmed by determinations in which the oxygen method of absorption was used, two independent observations giving 1.04 and 1.03 as the percentage of argon in atmospheric nitrogen.

Determinations of the density of argon prepared by means of oxygen, and of argon prepared by means of magnesium were made. A single determination of the gas obtained by the first method gave 19.7, and the mean of three results obtained with gas prepared by the second process was 19.88.

The spectrum of argon has been examined by Crookes, and forms the subject of a separate communication. Seen in a vacuum tube of about 3 mm. pressure, it consists of a great number of lines, distributed over almost the whole visible field. Two lines are specially characteristic; they are less refrangible than the red lines of hydrogen or lithium, and serve well to identify the gas when examined in this way. The wave lengths of these lines are 696.56 and 705.64×10^{-6} mm. Besides these red lines, a bright yellow line, more refrangible than the sodium line, occurs at 603.84 . A group of five green lines occurs next, of which the second is perhaps the most brilliant, and has the wave length 561.00 . There is next a blue line of wave length 470.2 , and then five strong violet lines of which the fourth is the most brilliant, and has the wave length 420.0 .

When the current is passed from the induction coil in one direction, that end of the capillary tube next the positive pole appears of a redder,

and that next the negative of a bluer hue. There are, in effect, two spectra, which Crookes has succeeded in separating to a considerable extent. A phenomenon of this order has been attributed to the presence of two gases, and the conclusion would follow that argon is in reality a mixture of two gases, which have as yet not been separated. This conclusion is, if true, of great importance, and experiments are in progress to test it by other physical methods.

Crookes and also Schuster have proved the identity of the chief lines of the spectrum of gas separated from air-nitrogen by aid of magnesium with that remaining after sparking air-nitrogen with oxygen, in presence of caustic soda solution.

The solubility of argon in water has been already alluded to, and special experiments were tried to determine the degree of solubility. The course marked out by Bunsen was followed. The solubility of the gas isolated by means of oxygen was found to be 3·94 per 100 of water at 12°, and argon prepared by means of magnesium gave a result of 4·05 per 100 of water. The solubility is therefore about $2\frac{1}{2}$ times that of nitrogen. The fact that the gas is more soluble than nitrogen led to the expectation of finding it in increased proportion in the dissolved gases of rain water, an anticipation which experiment confirmed.

The behaviour of the gas at low temperatures was examined by Olszewski, whose results are published separately. The following tables are given for convenience of reference.

Vapour Pressures.

Temp.	Pressure.	Temp.	Pressure.	Temp.	Pressure.
-186·9°	740·5 mm.	-136·2°	27·3 atms.	-129·4°	35·8 atms.
-139·1	23·7 atms.	-135·1	29·0 „	-128·6	38·0 „
-138·3	25·3 „	-134·4	29·8 „	-121·0	50·6 „

Gas	Critical temperature.	Critical pressure.	Boiling point.	Freezing point.	Freezing pressure.	Density of gas.	Density of liquid at boiling point.	Colour of liquid.
	°	atms.	°	°	mm.			
Hydrogen, H ₂	below 220·0	20·0	?	?	?	1·0	?	Colourless.
Nitrogen, N ₂	-146·0	35·0	-194·4	-214·0	60	14·0	0·885	„
Carbonic oxide, CO.....	-139·5	35·5	-190·0	-207·0	100	14·0	?	„
Argon, A ₁	-121·0	50·6	-186·9	-189·6	?	19·9	about 1·5	„
Oxygen, O ₂	-118·8	50·8	-182·7	?	?	16·0	1·124	Bluish.
Nitric oxide, NO....	-93·5	71·2	-153·6	-167·0	138	15·0	?	Colourless.
Methane, CH ₄	-81·8	54·9	-164·0	-185·8	80	8·0	0·415	„

In order to decide regarding the elementary or compound nature of argon, experiments were made on the velocity of sound in it. From these the ratio of the specific heat at constant pressure to that at constant volume was deduced in the well-known manner. The accuracy of the apparatus used was tested by preliminary observa-

tions with air, carbonic anhydride, and hydrogen, which gave results in agreement with those of other observers. Five series of measurements were then made with a sample of gas of density 19.86, and the ratio C_p/C_v of the specific heats found was 1.644. This is practically the theoretical ratio, 1.66, for a monatomic gas, that is, a gas in which all energy imparted to it at constant volume is expended in effecting translational motion. The only other gas of which the ratio of specific heats has been found to fulfil this condition is mercury at a high temperature.

A great number of attempts were made to induce chemical combination with the argon obtained by use of magnesium, but without any positive result. The following substances were tried under different conditions, but without effect:—(a) Oxygen in presence of caustic alkali, (b) hydrogen, (c) chlorine, (d) phosphorus, (e) sulphur, (f) tellurium, (g) sodium, (h) fused and red-hot caustic soda, (i) soda-lime at a red heat, (j) fused potassium nitrate, (k) sodium peroxide, (l) persulphides of sodium and calcium, (m) nitro-hydrochloric acid, (n) bromine water, (o) a mixture of potassium permanganate and hydrochloric acid, (p) argon is not absorbed by platinum-black. Argon is, therefore, most astonishingly indifferent, inasmuch as it is not attacked by elements of very opposite character ranging from sodium and magnesium on the one hand, to oxygen, chlorine, and sulphur on the other. It will be necessary to try whether the inability of argon to combine at ordinary or at high temperatures is due to the instability of its possible compounds, except when cold. Mercury vapour at 800° would present a similar instance of passive behaviour.

The authors finally discuss the probable nature of the gas or gases which they have succeeded in separating from atmospheric air, and which has been provisionally named *argon*. It has been shown that argon is present in the atmosphere, and is not manufactured during the process of separation, and it is practically certain that the argon prepared by means of electric sparking with oxygen is identical with argon prepared by means of magnesium. That argon is an element or mixture of elements, may be inferred from the observations on the ratio of the two specific heats. For if argon molecules are di- or polyatomic, the atoms acquire no relative motion, even of rotation, a conclusion improbable in itself and one postulating the sphericity of such complex groups of atoms. But a monatomic gas can be only an element, or a mixture of elements; and hence it follows that argon is not of a compound nature. Argon is approximately 20 times as heavy as hydrogen, that is, its molecular weight is 20 times as great as that of hydrogen, or 40. But its molecule is monatomic, hence its atomic weight, or, if it be a mixture, the mean of the atomic weights of the elements in that mixture, taken for the proportion in which they are present, must be 40. There is evidence both for and against the hypothesis that argon is a mixture; for the present, however, the balance of evidence seems to point to simplicity.

If argon is a single element of the atomic weight 40, no vacant place can be assigned to it in the periodic system, and there is then

reason to doubt whether the periodic classification of the elements is complete; whether, in fact, elements may not exist which cannot be fitted among those of which it is composed. On the other hand, if argon is a mixture of two elements, they might find a place in the eighth group, one after chlorine and one after bromine. It would be difficult, however, in this case to account for the heavier element having escaped detection. If it be supposed that argon belongs to the eighth group, then its properties would fit fairly well with what might be anticipated. For the series which contains



might be expected to end with an element of monatomic molecules of no valency, that is, incapable of forming a compound, or if forming one, being an octad; and it would form a possible transition to potassium, with its monovalence, on the other hand.

As for the physical condition of argon, that of a gas, we possess no knowledge why carbon, with its low atomic weight, should be a solid, while nitrogen is a gas, except in so far as we ascribe molecular complexity to the former and comparative molecular simplicity to the latter. Argon, with its comparatively low density and its molecular simplicity, might well be expected to rank among the gases. And its inertness, which has suggested its name, sufficiently explains why it has not previously been discovered as a constituent of compound bodies.

Assuming provisionally that it is not a mixture, the symbol A is suggested for this element.

In addenda by Ramsay, further determinations of the density of argon are given, the general mean being 19.900. The value of R in the gas equation $R = pv/T$, has been determined between -89° and $+248^\circ$. The numbers show that argon undergoes no molecular change within these limits of temperature. Further determinations of the ratio of the two specific heats were also made, the general mean being 1.643.

H. C.

A Singular Case of Metallic Precipitation. By J. B. SENDERENS (*Bull. Soc. Chim.*, 1894, [3], 11, 424—426; compare *Abstr.*, 1895, ii, 315).—When bright lead is immersed in a solution of lead nitrate containing from 10 to 400 grams per litre, and protected from access of air, metallic lead is gradually precipitated on it in well-defined crystals, just as on iron or zinc. A certain amount of lead nitrite is produced at the same time, and in weaker solutions forms the exclusive product, being deposited in yellow crystals in place of those of the metal.

The lead crystals form plates from 1 to 4 mm. in diameter, and are chemically pure, but they rapidly oxidise in air to the hydroxide, so that a crystallographic examination is impracticable. When kept undisturbed in the original liquid, the metallic crystals are gradually converted into a *basic nitrate*, which crystallises in large, white tufts of silky needles as much as 2 cm. in length.

The precipitation of the lead is not due to local electrolytic action set up by metallic impurities, for precisely the same result is ob-

tained with pure lead made by reducing, by means of sugar-charcoal, litharge prepared from the pure nitrate (compare, however, *loc. cit.*); moreover, the precipitation does not occur in solutions of lead acetate, as would be the case if it were due to this cause. J. N. W.

Double Halogen Salts of Ammonium and Copper. By HORACE L. WELLS and E. B. HURLBURT (*Zeit. anorg. Chem.*, 1895, **10**, 157—160, and *Amer. J. Sci.*, 1895, [3], **50**, 390—393).—The *chloride*, $4\text{NH}_4\text{Cl} \cdot \text{Cu}_2\text{Cl}_2$, is obtained by cooling a mixed solution of its component salts containing hydrochloric acid, copper wire being placed in the liquid; a large excess of ammonium chloride must be used; it crystallises in colourless prisms, which, on exposure to air, quickly turn brown and then green. The *chloride*, $4\text{NH}_4\text{Cl} \cdot 3\text{Cu}_2\text{Cl}_2$, is obtained when its component salts are dissolved in the proper proportions in dilute hydrochloric acid; it crystallises in lustrous, colourless dodecahedra, and is fairly stable on exposure to air, but gradually turns green.

The *bromide*, $4\text{NH}_4\text{Br} \cdot \text{Cu}_2\text{Br}_2$, obtained in a similar way to the corresponding chloride, crystallises in long, colourless prisms, and is much more stable than the corresponding chloride; on exposure to air, it gradually turns green. The *bromide*, $2\text{NH}_4\text{Br} \cdot \text{Cu}_2\text{Br}_2 + \text{H}_2\text{O}$, is obtained if an excess of cuprous bromide is present; it crystallises in lustrous, colourless rhombohedra, and is more stable than the preceding salt.

The *iodide*, $2\text{NH}_4\text{I} \cdot \text{Cu}_2\text{I}_2$, is the only salt obtained even when the components are employed in very different proportions.

E. C. R.

Formation of Nickel Carbonyl. By H. G. FREY (*Ber.*, 1895, **28**, 2512—2514).—Sodium decomposes ethylic oxalate into ethylic carbonate and carbonic oxide. When ethylic oxalate is added to finely divided nickel chloride and sodium, suspended in light petroleum, traces of nickel carbonyl are found in the gas which is evolved, but the amount present is so small that no liquid can be obtained.

Ferric chloride, when treated in the same way, gave no trace of iron carbonyl. A. H.

Double Salts of Cæsium Chloride with Chromium Trichloride and Uranyl Chloride. By HORACE L. WELLS and B. B. BOLTWOOD (*Zeit. anorg. Chem.*, 1895, **10**, 181—184; also *Amer. J. Sci.*, 1895, [3], **50**, 254—258).—The *chloride*, $2\text{CsCl} \cdot \text{CrCl}_3 + \text{H}_2\text{O}$, is obtained by saturating warm solutions of its component salts with hydrogen chloride, and corresponds with the double chlorides prepared by Neumann (*Abstr.*, 1888, 655). It crystallises in aggregates of small, reddish-violet crystals, is stable on exposure to air, does not give up its water of crystallisation at 100° , and dissolves slowly in water forming a green solution. The *chloride*, $2\text{CsCl} \cdot \text{CrCl}_3 + 4\text{H}_2\text{O}$, is obtained from a cold solution of its components by saturating it with hydrogen chloride, or by evaporation over sulphuric acid; it crystallises in green, monoclinic crystals, is somewhat hygroscopic, very easily soluble in water, and when heated at 110° loses $3\text{H}_2\text{O}$, and is converted into the above violet salt. The authors point out that whereas green chromium sulphate contains less water than the violet modification,

the reverse is the case with the double caesium salts, and that therefore probably the green colour of the salts is not due to the formation of basic salts and free acid, or of acid salts.

The *chloride*, $2\text{CsCl}, \text{UO}_2\text{Cl}_2$, prepared in a similar way to the above, corresponds with the double salts already described; it crystallises in beautiful yellow, rhombic leaflets. E. C. R.

Chemical Behaviour of Pyrites and Marcasite. By AMOS P. BROWN (*Proc. Amer. Phil. Soc.*, 1894, 33, 225—243). See Abstr., 1895, ii, 316.—The constitution here deduced for marcasite is the same as that given by Loczka (Abstr., 1895, ii, 20) for pyrites, namely,



L. J. S.

Mineralogical Chemistry.

A Graphitic Schist from Co. Donegal. By RICHARD J. MOSS (*Scient. Proc. Roy. Dublin Soc.*, 1893, **8**, N.S., 206—207).—A graphitic schist from Glendown, Letterkenny, with a lustre like graphite, but of a grayish tint, gave on analysis

H ₂ O (at 100°).	H ₂ O (on ignition).	C.	S.	Ash (less O for S).	Total.	Sp. gr.
0.98	3.68	3.15	4.03	87.89	99.73	2.662

The ash gave, together with traces of manganese and nickel,

SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	CaO.	MgO.	Na ₂ O.	K ₂ O.	Total.
58.91	19.87	7.40	4.86	1.63	3.54	3.73	99.94

L. J. S.

Wurtzite from Mies, Bohemia. By FRIEDRICH BECKE (*Tsch. Min. Mitth.*, 1894, **14**, 278—279).—Botryoidal and stalactitic schalenblende from near Mies, gave on analysis (by Heinisch)

S.	Zn.	Cd.	Fe.	Gangue.	Total.	Sp. gr.
30.23	65.84	1.02	0.45	1.11	98.65	3.672

This deficiency of about $1\frac{1}{2}$ per cent. is also to be noticed in the previous analysis by Gerstendörfer (*Ber. Akad. Wien*, **99**). In the above analysis, the atomic ratio Zn, &c. : S = 1.030 : 0.945, and for the excess of zinc, &c., is calculated 1.36 per cent. of oxygen; this would correspond with a mixture of 39.9 per cent. of wurtzite (ZnS), and 60.1 per cent. of wurtzite. Under the microscope, however, there is no indication of such a mixture, and the substance consists of fibres giving straight extinction, and with positive double refraction.

L. J. S.

Artificial Cinnabar. By J. A. IPPEN (*Tsch. Min. Mitth.*, 1894, **14**, 114—120).—Powdered cinnabar heated with sodium sulphide in a sealed tube at 80°, gave crystals of cinnabar, and also a black deposit containing small, black crystals of cinnabar. In another experiment,

where black precipitated mercuric sulphide was exposed to sunlight for two months in a sealed tube with sodium sulphide, the temperature never exceeding 45° , small, well-developed crystals of cinnabar were formed; with hydrochloric acid under the same conditions no cinnabar was formed. Cinnabar is shown to be slightly soluble in sodium carbonate solution.

L. J. S.

Nickeliferous Pyrites. By WILLIAM L. GOODWIN (*Canadian Rec. Sci.*, 1893, 5, 346—347).—In the Murray mine, Sudbury, Ontario, are grey nodules of a nickel ore resembling mispickel in colour and appearance. Analysis gave

Fe.	Ni (and Co?).	S.	Insol.	Total.
37.45	4.82	44.26	9.92	96.45

Calculated to FeS_2 and NiS_2 , the analysis shows an excess of 3.33 per cent. of iron, which is accounted for by the presence of the associated magnetite, pyrrhotite, and hornblendic matrix.

L. J. S.

Skleroklase (Sartorite) from Binn. By HEINRICH BAUMHAUER (*Ber. Akad. Berlin*, 1895, 243—252).—The results of the measurement of four crystals from the Binnenthal are given, numerous new forms being noted. Analysis of one small crystal gave

S.	Pb.	As.	Total.	Sp. gr.
25.26	46.08	26.28	97.62	5.05

The formula deduced is $3(\text{PbS}, \text{As}_2\text{S}_3) + 2\text{PbS}, \text{As}_2\text{S}_3$, this being near to von Waltershausen's formula in which there is 3.124, instead of 3 of the first molecule. vom Rath's formula, $\text{PbS}, \text{As}_2\text{S}_3$, is the one usually accepted.

L. J. S.

Safflorite from Nordmark, Sweden. By S. A. HJALMAR SJÖGREN (*Bull. Geol. Inst., Upsala*, 1894, 2, 68—71).—This mineral occurs at the Kogrufva, in a dolomitic calcite, and associated with chondrodite, tremolite and blende. It is tin-white, and usually massive, but sometimes in crystals; the crystallographic constants, which have not before been determined for this mineral, are given. Sp. gr. 7.41. Analysis by Mauzelius gave

Fe.	Co.	Ni.	As.	S.	Pb (+ Cu).	Total.
15.28	12.99	0.20	71.13	0.68	0.33	100.61

This gives the formula $(\text{Fe}, \text{Co})\text{As}_2$, or nearly $\text{FeAs}_2, \text{CoAs}_2$. Although the composition is half way between that of safflorite and löllingite, the author considers this mineral to belong to the former, as the crystals differ from those of the latter.

L. J. S.

Fiorite. By AUGUSTIN A. DAMOUR (*Bull. Soc. fran. Min.*, 1894, 17, 151—153).—This opal, from Fiora, Tuscan, is either white and translucent, with a satiny and pearly lustre (Analysis I), or white and opaque (II). On heating, it gives off acid water, which etches glass; when powdered and moistened it also gives an acid reaction.

Both before and after ignition, it is almost wholly dissolved by caustic potash.

	SiO ₂ .	H ₂ O and SiF ₄ . (Loss on ignition).	Al ₂ O ₃ and Fe ₂ O ₃ .	Total.	Sp. gr.
I.	96.70	2.90	0.40	100.00	2.17
II.	96.59	3.10	0.31	100.00	2.19

This suggests that fluorite has been formed by the action of water on silicon fluoride, some hydrogen silicofluoride being enclosed in the separated silica.

L. J. S.

Artificial Martite. By CHARLES FRIEDEL (*Bull. Soc. fran. Min.*, 1894, **17**, 150—151).—Martite is now usually considered to be hæmatite pseudomorphous after magnetite. On heating crystals of magnetite, weighing 0.4499 gram, over the blowpipe for four or five hours, there was a gain in weight of 0.0158 gram (calculated for change from Fe₃O₄ to Fe₂O₃ = 0.0155). By this treatment, the crystals have lost their magnetic properties, but are only slightly changed in outward aspect, having become slightly rough on the surface, and of a gray colour. The material has therefore been transformed from magnetite to hæmatite.

L. J. S.

Pyroaurite from the Mossgrufva, Nordmark, Sweden. By S. A. HJALMAR SJÖGREN (*Bull. Geol. Inst., Upsala*, 1894, **2**, 59—63).—Pyroaurite occurs in the manganiferous dolomite of this mine as thin, yellow to yellowish-brown, crystalline scales with a round or hexagonal outline. The crystal angles are near to those of chalcophanite, but the crystals are hexagonal with pyramidal hexahedrism; optically uniaxial, with optical anomalies. On heating, the mineral is infusible, and retains its yellow colour; after ignition, it is strongly magnetic, before, only slightly so; sp. gr. 2.07; analysis by Mauzelius, on a small amount of material dried at 108°, gave

Fe ₂ O ₃ .	MnO.	MgO.	H ₂ O.	Insol.	Total.
22.0	4.5	34.8	36.1	0.5	97.9

This agrees nearly with the pyroaurite formula, with part of the Mg replaced by Mn, namely, Fe₂O₃.6(Mg,Mn)O.15H₂O; some of the iron may be ferrous.

L. J. S.

Artificial Crystallised Carbonates. By LÉON BOURGEOIS (*Bull. Soc. fran. Min.*, 1894, **17**, 79—81).—The author points out that his humid methods for producing crystallised carbonates, such as calcite, strontianite, &c. (*Abstr.*, 1887, 221), are identical with those of Bunsen (*Annalen*, 1847, **65**, 71).

L. J. S.

Fluid Enclosures in Gypsum. By S. A. HJALMAR SJÖGREN (*Bull. Geol. Inst., Upsala*, 1893, **1**, 277—281, and *Geol. För. Förh.*, 1893, **15**, 136).—In large crystals of gypsum from Girgenti, Sicily, large fluid enclosures were present; from the largest cavity, 3 c.c. of a neutral liquid were obtained, hydrogen sulphide escaping from the cavity at not very great pressure. The liquid contained 4.02 per cent. of solids, which had the composition (anal. by Mauzelius)

K ₂ SO ₄ .	Na ₂ SO ₄ .	CaSO ₄ .	NaCl.	MgCl ₂ .
3·7	11·4	9·7	66·2	9·0

This is compared with sea water and with the water of the Kaiserquelle at Aix-la-Chapelle.

Two views have been put forward to account for the origin of the sulphur of the Sicilian deposits: one supposes it to have been formed by the reducing action of organic matter on gypsum in isolated lagoons; the other, that it has been deposited with the gypsum from spring waters containing hydrogen sulphide; the latter view is supported by the above analysis.

L. J. S.

Artificial Anhydrite. By REINHARD BRAUNS (*Jahrb. f. Min.*, 1894, ii, 257—264).—Anhydrite has been artificially formed by fusing together calcium sulphate and chloride, and by heating gypsum in sealed tubes with chlorides, or by digesting it with hot sodium chloride solution; these processes would, however, not account for the formation of the large beds of anhydrite found in nature.

In the author's experiments, a large drop of a saturated solution of sodium and potassium chlorides is placed on a microscope slide, at its side a drop of calcium chloride solution, and, opposite this, a drop of magnesium sulphate solution; the two drops are then brought into contact by a narrow path, and allowed to evaporate. As diffusion takes place, small prisms of anhydrite are deposited, and, here and there, gypsum. On removing the salt crystals and adding water, the anhydrite crystals are immediately corroded, and gradually disappear, and, on allowing this mixture to evaporate, gypsum, and not anhydrite, crystals are formed. In case the amount of water added is not enough to completely dissolve the anhydrite, gypsum crystals are deposited around the corroded forms; or sometimes, when the gypsum crystals do not grow on the surface of the anhydrite, but near to it, they may be seen to grow at the expense of the anhydrite.

Calcium sulphate is, therefore, one of those substances which crystallise from saline solutions in compounds poor in water, such solutions having the same effect as an increase in temperature. Instances of a relation similar to that of gypsum and anhydrite, are epsomite and kieserite, and glauberite and thenardite; moreover, the second members of each of these pairs crystallise together in nature from saline solutions.

L. J. S.

Serpierite, Lautite, and Pseudobrookite. By AUGUST FRENZEL (*Tsch. Min. Mitth.*, 1894, 14, 121—130).—*Serpierite*.—This mineral, which occurs at Laurion, Greece, in bushy groups of blue, orthorhombic crystals, has not before been analysed. Sp. gr. 2·52; analysis gave

CuO.	ZnO.	CaO.	SO ₃ .	H ₂ O.	Total.
36·12	13·95	8·00	24·29	16·75	99·11

Formula: 3(CuO,ZnO,CaO),SO₃ + 3H₂O. At 100° 1·26 per cent. of water is given off; at 285° the powdered mineral becomes black.

Lautite.—A new find of this mineral has been made at the old locality, Lauta, Marienberg, Saxony; it occurs as radiating aggre-

gates, and, from its appearance, it cannot be a mixture, as has been supposed. Analysis gave

Cu.	As.	S.	Total.	Sp. gr.
36·10	45·66	17·88	99·64	4·91

This leads to the formula previously adopted by Frenzel, namely, CuAsS . Some of the previous analyses show 12 per cent. of silver.

Pseudobrookite.—The formula which has been derived for the natural mineral is $2\text{Fe}_2\text{O}_3, 3\text{TiO}_2$; but to the artificial mineral has been given the formula, $\text{Fe}_2\text{O}_3, \text{TiO}_2$ (Abstr., 1893, ii, 18). Analysis of the material from the original locality, Aranyer Berg, Transylvania, gave (Frenzel) I and (Traube) II.

	TiO_2 .	Fe_2O_3 .	MgO .	SiO_2 .	Total.
I.	41·27	54·24	2·09	1·66	99·26
II.	41·46	56·45	1·0	1·29	100·20

Deducting magnesia and silica as representing admixed szaboite, these analyses give the formula $2\text{Fe}_2\text{O}_3, 3\text{TiO}_2$. Experiments of Traube's are given by which he tested the methods of separating TiO_2 and Fe_2O_3 .

L. J. S.

Hautefeullite, a New Mineral from Bamle, Norway. By LÉOPOLD MICHEL (*Bull. Soc. fran. Min.*, 1893, 16, 38—40).—In the greyish apatite veins in the gabbro of Odegården, are greenish nodules consisting of a mixture of wagnerite and apatite, in which the new mineral was found together with crystals of apatite, pyrites and monazite. The colourless, transparent, monosymmetric crystals form lamellar and radial aggregates: cleavage parallel to the plane of symmetry perfect; sp. gr. 2·435; plane of the optic axes parallel to the plane of symmetry, 2E about 88° , 2V = $54^\circ 23'$ for yellow light. Analysis gave

P_2O_5 .	MgO .	CaO .	H_2O .	Total.
34·52	25·12	5·71	34·27	99·62

This gives the formula $(\text{Mg}, \text{Ca})_3(\text{PO}_4)_2 + 8\text{H}_2\text{O}$. The mineral differs from bobierite in containing calcium, and in the optical characters.

L. J. S.

Caryinite. By S. A. HJALMAR SJÖGREN (*Bull. Geol. Inst., Upsala*, 1894, 2, 113—118).—The only previous analysis of this mineral has been shown to have been made on impure material, the specimens having been mixed with calcite and berzeliite, into the latter of which caryinite is readily altered. A new find of the mineral at the old locality, Långban, Sweden, has rendered it possible to analyse pure, fresh material, and to determine, by means of the cleavage and optical characters, that the mineral is orthorhombic. The massive, nut-brown mineral occurs in fissures with schefferite, rhodonite and hedyphane; sp. gr. 4·29; analysis by Mauzelius, on material dried at 110° , gave

As_2O_5 .	P_2O_5 .	PbO .	FeO .	MnO .	MgO .	BaO .	CaO .
49·78	0·19	9·21	0·54	18·66	3·09	1·03	12·12
		K_2O .	Na_2O .	H_2O .	Total.		
		0·37	5·16	0·53	100·68		

Also traces of V_2O_5 (?) and Cl. If the water exists with the bases as H_2 , the formula deduced is $10RO, 3As_2O_5$; if, however, it exists in the group $2(HO-R'')$ the formula is $3RO, As_2O_5$. The original analysis of this mineral showed neither alkalis nor water. Compare soda-berzeliite below.

L. J. S.

Soda-berzeliite from Långban, Sweden. By S. A. HJALMAR SJÖGREN (*Bull. Geol. Inst., Upsala*, 1894, 2, 118—121).—This new variety of berzeliite differs from berzeliite in outward appearance by its orange-yellow to fire-red colour; it is usually massive, but sometimes occurs as crystals (icositetrahedra). Sp. gr. 4.21. Analysis by Mauzelius gave

As_2O_5 .	V_2O_5 .	FeO.	MnO.	CaO.	MgO.	K_2O .	Na_2O .	H_2O .	Total.
52.90	0.24	0.38	21.41	18.34	0.72	0.09	5.05	0.40	99.53

together with traces of Sb_2O_3 and Cl, and about $\frac{1}{2}$ per cent. of insoluble matter. This analysis is very similar to that of caryinite (see preceding abstract), and in the same manner according as the water is assumed to be combined with the acids or the bases the formula deduced is $10RO, 3As_2O_5$, or $3RO, As_2O_5$ respectively. As these two minerals differ crystallographically, berzeliite being cubic and caryinite orthorhombic, they may have different formulæ ($10RO, 3As_2O_5$ and $3RO, As_2O_5$), or they may have the same formula and be dimorphous, or thirdly the presence of lead in caryinite may be essential.

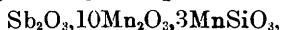
Igelström's pyrrhoarsenite (Abstr., 1895, ii, 76) resembles soda-berzeliite in some respects.

L. J. S.

Långbanite from the Sjögrufva, Sweden. By S. A. HJALMAR SJÖGREN (*Bull. Geol. Inst., Upsala*, 1894, 2, 96—97).—This mineral, before only known from the Långban mines, has been found at the Sjö mine in a mixture of rhodonite, manganophyllite, braunite and calcite; it is generally in lamellar masses, but sometimes shows hexagonal outlines and a distinct basal cleavage. In very thin splinters, it is sub-translucent with a red colour; sp. gr. 4.60. Analysis by Mauzelius gave

Sb_2O_3 .	Fe_2O_3 .	SiO_2 .	MnO_2 .	MnO.	CaO.	MgO.	H_2O .	Total.	O.
12.51	13.98	12.82	24.36	32.22	2.40	1.11	0.52	99.92	3.09

This gives the ratio $Sb_2O_3 : Fe_2O_3 : RO_2 : RO = 0.087 : 0.177 : 1 : 1.07$. As before (Abstr., 1893, ii, 421) the oxides $R''O$ and $R''O_2$ may be brought together as R'''_2O_3 , and the substances considered as an isomorphous mixture of the three groups in the formula $mSb_2O_3 + nFe_2O_3 + pR''R'''O_3$, where, in this case $m : n : p = 10 : 20 : 115$. The fairly constant amount of Sb_2O_3 shown in previous analyses would, however, tell against this improbable isomorphous mixture. The mineral here analysed closely resembles in appearance and composition Sjögren's B type of långbanite from Långban, and may be represented by the empirical formula $Sb_2O_3, 9Mn_2O_3, 5MnSiO_3$, whilst the A type from Långban may be represented by



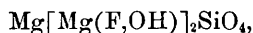
where Mn_2O_3 is partly replaced by Fe_2O_3 , and MnSiO_3 by CaSiO_3 and MgSiO_3 . L. J. S.

Apophyllite from Algeria. By LOUIS GENTIL (*Bull. Soc. fran. Min.*, 1894, 17, 11—28).—In an altered andesite at Bou Serdoun, Collo, are cavities, containing apophyllite and other minerals. The crystals show optical anomalies; analyses gave

SiO_2 .	CaO .	MgO .	K_2O .	Na_2O .	H_2O .	Total.	Sp. gr.
52.32	25.30	0.57	4.83	0.80	16.66	100.48	2.372

At 100° there is a loss of 0.33 per cent. of water; fluorine was absent (*Abstr.*, 1894, ii, 421). The associated minerals and the rock are described at length. L. J. S.

Proectite, a New Mineral of the Humite Group. By S. A. HJALMAR SJÖGREN (*Bull. Geol. Inst., Upsala*, 1894, 2, 99—105).—Two fragments of crystals from Nordmark, Sweden, were found to differ from the other brownish-grey humite minerals of the same locality in their crystal angles and optical characters: the crystallographic constants are approximately $a:b:c = 1.0803:1:1.8862$; $\beta = 90^\circ$; the vertical axis (c) is, therefore, one-third of that of clinohumite. Penfield and Howe (*Abstr.*, 1894, ii, 241) have predicted the existence of a member of the humite group having the composition



and the axial ratios $a:b:c = 1.086:1:1.887$; $\beta = 90^\circ$. Owing to lack of material, the mineral has not been analysed. L. J. S.

Composition of Chondrodite, Humite and Clinohumite, from Nordmark. By S. A. HJALMAR SJÖGREN (*Bull. Geol. Inst., Upsala*, 1894, 2, 39—54).—In a previous paper (*Bull. Geol. Inst., Upsala*, 1892, 1, 16—40) are given the results of the crystallographic and optical measurements of these minerals from a new locality, the Kogrufva, Sweden; the mode of occurrence and associations are strikingly similar to those at the Tilly Foster Iron Mine, N.Y. Seven duplicate analyses by R. Mauzelius, lead to the same formulæ as those given by Penfield and Howe (*Abstr.*, 1894, ii, 241). Potassium, sodium, and titanium were found in small quantities, and there is a slight variation in the amount of water shown in the analyses, owing, when too high, to the partial alteration of the mineral to serpentine, and, when too low, to the difficulty of driving off all the water. The ratio of $\text{F}:\text{OH}$ was always about 1:1. On heating chondrodite in dry hydrogen chloride (Clarke's method), the amount of magnesium rendered soluble, agreed with that required by the assumption of the existence of the group MgOH . Structural formulæ showing the relation to olivine are given. L. J. S.

Soda-richterite from Långban, Sweden. By S. A. HJALMAR SJÖGREN (*Bull. Geol. Inst., Upsala*, 1894, 2, 71—77).—This mineral occurs with rhodonite in rather coarsely crystalline, columnar aggregates of an azure-blue or gray to grayish-violet colour. The cleavage

angle of $56^{\circ} 27'$, and the optical characters show it to belong to the hornblende group. I gives the analysis by Mauzelius of the blue variety, sp. gr. 3.05, and II of the grayish-violet, sp. gr. 3.10.

	SiO ₂ .	FeO.	MnO.	CaO.	MgO.	K ₂ O.	Na ₂ O.	H ₂ O.	F. (less O for F).	Total.
I.	56.25	0.15	6.49	5.44	21.89	1.60	6.17	1.56	0.15	99.64
II.	54.76	0.21	12.71	5.83	17.82	1.65	4.02	2.77	0.09	99.82

Calculating the water, which only goes off at a high temperature, as H₂ with the metals, the analyses reduce to the metasilicate formula. A sample of the blue variety lost 3.37 per cent. on ignition, and from the powder was extracted by soda solution 13.38 per cent. of SiO₂, this corresponding with 3.99 per cent. of water in H₂SiO₃. The above analyses do not reduce to the formula, CaMg₃Si₄O₁₂, sometimes given for non-aluminous amphiboles.

The original richterite of Breithaupt is shown to have been wrongly described.

L. J. S.

New Analyses of Chloromelanite. By AUGUSTIN A. DAMOUR (*Bull. Soc. fran. Min.*, 1893, 16, 57—59).—Several ancient stone axes with a density varying from 3.55 to 3.60 were seen to contain varying amounts of garnet in the dark green matrix; the latter, on being separated, gave the following analyses.

	SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	CaO.	MgO.	Na ₂ O.	Total.	Sp. gr.
Mexico	56.57	17.21	8.86	4.44	2.12	10.70	99.90	3.37
Antioch. . . .	55.01	9.99	10.09	12.00	5.23	7.48	99.80	3.36
Lyons	56.00	13.19	13.90	3.71	1.88	10.75	99.43	3.43
Carcassonne	57.75	14.85	9.52	3.15	1.81	11.76	98.87	3.40

Chloromelanite may be considered to be a ferruginous jadeite; both these minerals, after fusion, are decomposed by hot hydrochloric acid without gelatinisation. The association of garnet with chloromelanite constitutes a rock resembling eclogite.

L. J. S.

Andradite Garnet from Algeria. By LOUIS GENTIL (*Bull. Soc. fran. Min.*, 1894, 17, 269—272).—This garnet occurs near Cape Bou-Garoune, Constantine, in a vein of hæmatite and quartz with ilvaite, limestone, green pyroxene, and perhaps bustamite. The small dodecahedral crystals are yellowish to dark brown, and show optical anomalies. It is easily attacked by hot, strong hydrochloric acid; analysis gave

SiO ₂ .	Fe ₂ O ₃ .	Al ₂ O ₃ .	CaO.	Mn.	MgO.	K ₂ O.	Total.
36.03	30.94	0.27	32.58	trace	0.48	0.17	100.47

This gives the usual formula 3CaO,Fe₂O₃,3SiO₂. On ignition, there is a loss of 1.60 per cent., probably due to reduction.

L. J. S.

Artificial Ægirine. By HELGE BÄCKSTRÖM (*Bull. Soc. fran. Min.*, 1893, 16, 130—133).—A leucite-phonolite rich in hæüyne was fused and allowed to cool slowly for three days; the colourless glass thus produced contained microlites of oligoclase and nepheline, and

numerous crystals of a yellow pyroxene, which agree in their optical characters with ægirine. A mixture of quartz, ferric oxide, and sodium carbonate, in the proportions given by the ægirine formula, when treated in the same way, gave a mass largely consisting of prismatic crystals of ægirine, with some yellow glass, hæmatite scales, and probably felspar.

L. J. S.

Composition of Canadian Limestones and Dolomites. By BERNARD J. HARRINGTON (*Canadian Rec. Sci.*, 1894, 6, 27—32).—The author gives analyses of 18 limestones and dolomites from various geological horizons in Canada.

L. J. S.

Process of formation of Dolomitic Rock. By CONSTANTIN KLEMENT (*Bull. Soc. Belge Geol.*, 1895, 9, 3—23, and *Tsch. Min. Mitth.*, 1895, 14, 526—544).—After reviewing the different theories of the origin of dolomite, the author points out that dolomite deposits are often in the form of coral reefs, and that corals consist of aragonite. His experiments show that solutions of magnesium salts act much more readily on aragonite than on calcite. When powdered aragonite (crystals, corals, and artificial) is warmed with magnesium sulphate in a concentrated solution of sodium chloride, the action begins at about 60°, and increases with the temperature, until at 91° there is a maximum yield of about 42 per cent. of magnesium carbonate. Experiments were made with solutions of different concentrations, and of different salts. It is shown, by the action of dilute acids, that the product formed consists of a mechanical mixture of calcium and magnesium carbonates; but owing to the tendency of dolomite to crystallise, such a mixture would be gradually converted into dolomite. The conditions of these experiments would be those which exist in the isolated lagoons of coral islands.

L. J. S.

Lower Carboniferous Volcanic Rocks of East Lothian. By FREDERICK H. HATCH (*Trans. Roy. Soc., Edin.*, 1893, 37, 115—126).—Several analyses are given of the lower, basic lavas (basalts free from felspar), of the upper, more acid lavas (trachytes), and of the material filling the volcanic vents; all being of lower carboniferous age. I is of the limburgite of Whitelaw Hill; it is composed of olivine, augite, magnetite, glassy matter, and probably nepheline; sp. gr. 3·03. II is of the phonolite of the volcanic vent of Traprain Law; this consists of sanidine, nepheline, and green soda-augite, the nepheline being largely converted into zeolites; sp. gr. 2·588.

	SiO ₂ .	TiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	FeO.	MnO.	CaO.	MgO.
I.	40·2	2·9	12·8	4·0	10·4	—	10·4	11·9
II.	56·8	0·5	19·7	2·2	3·5	0·2	2·2	0·4
			Na ₂ O.	K ₂ O.	Loss on ignition.	Total.		
I.			2·7	0·8	3·4	99·5		
II.			4·3	7·1	2·5	99·4		

Limburgite has not before been recorded in the British Isles, and phonolite only at the Wolf Rock.

L. J. S.

Borolanite, an Igneous Rock. By J. J. HARRIS TEALL and JOHN HORNE (*Trans. Roy. Soc., Edin.*, 1893, **37**, 163—178).—This intrusive, igneous rock, from near Loch Borolan in Sutherland, consists principally of orthoclase and melanite garnet, with plagioclase, pyroxene, biotite, and alteration products of nepheline; it is thus related to the clæolite-syenites. I gives a bulk analysis of the rock, and II the portion soluble in hydrochloric acid. III is of a peculiar blue substance which is decomposed by acids, and is probably the alteration product of a member of the sodalite group.

	SiO ₂ .	TiO ₂ .	SO ₃ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	FeO.	MnO.	BaO.	CaO.
I.	47·8	0·7	0·4	20·1	6·7	0·8	0·5	0·8	5·4
II.	69·3	—	—	16·8			—	—	3·9
III.	36·1	—	5·9	28·4	—	—	—	—	3·2

	MgO.	Na ₂ O.	K ₂ O.	Loss on ignition.	Total.
I.	1·1	5·5	7·1	2·4	99·3
II.	0·3	4·6	1·7	2·4	99·0
III.	—	16·2	1·8	—	91·6

L. J. S.

Analyses of Augite and Nepheline-leucite-tephrite from Bohemia. By J. E. HIBSCH (*Tsch. Min. Mitth.*, 1894, **14**, 95—113).—Fourteen analyses of various igneous rocks from the Bohemian Mittelgebirge are given. I is of a nepheline-leucite-tephrite from Falkenberg, and II of the large augite crystals of the same rock; both analysed by F. Pfohl.

	SiO ₂ .	TiO ₂ .	P ₂ O ₅ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	FeO.	MnO.	CaO.
I.	47·83	2·27	1·33	16·09	4·32	3·62	trace	10·68
II.	45·67	0·62	—	9·04	7·46	2·00	—	21·78

	MgO.	K ₂ O.	Na ₂ O.	H ₂ O (combined).	Moisture.	Total.	Sp. gr.
I.	5·53	4·05	4·46	0·24	0·05	100·47	2·858
II.	12·09	0·56	1·25	0·31	—	100·78	3·37

The spectroscope showed Sr and Li in I.

L. J. S.

Argon and Helium in Mineral Waters. By CH. BOUCHARD (*Compt. rend.*, 1895, **121**, 392—394).—The gas evolved from the sulphur waters of the Pyrenees consists mainly of nitrogen. The gas from the spring at Raillère, however, contains argon and helium, and that from the two springs at Bois contains helium, and apparently another element also, the spectrum of which is characterised by red and orange-red lines.

C. H. B.

Composition of Water of the Pacific. By CAMILLE CHABRIÉ (*Bull. Soc. fran. Min.*, 1894, **17**, 220—222).—A sample of water taken from the surface of the Pacific at "latitude 12 hours north of Paris," contained, in a litre, 24·27 grams of chlorine and 3·056 grams of SO₄. Bromine and iodine are absent or present only in traces. The water

is neutral, and has a sp. gr. of 1.028 at 26°. The amount of chlorine in this water is greater than that in the water of other oceans.

L. J. S.

Physiological Chemistry.

Respiratory Metabolism. By WILHELM FILEHNE and H. KIONKA (*Pflüger's Archiv*, 1895, 92, 201—248).—Geppert and Zuntz (*ibid.*, 42, 189) have shown that during muscular work, in spite of the increased respiratory exchange, the blood gases remain practically unaltered. They consider that this constancy is regulated by nervous action, and one of the questions investigated in the present research is the discovery of the nerve channels, and the results of dividing them. Rabbits and dogs were used; muscles were thrown into tetanus by electrical stimulation, and the expired air and blood gases analysed by Zuntz's methods. Observations are also recorded on body weight and temperature.

The result of cutting the nerves of the tetanised muscles is that muscular work causes a fall in the amount of oxygen in the aortic blood; there is also a small diminution in the amount of carbonic anhydride. But when the vagi are also divided, there is a marked rise in the latter gas, and a fall in the amount of oxygen; the vagi are supposed to be the chief nervous channels in question, experiments leading to the conclusions that it is on the vagal terminations in the lungs that the venous blood specially acts, and thus secondarily on the respiratory centre, and further that the diminution of oxygen is a more important factor in exciting dyspnoëic symptoms than increase of carbonic anhydride. On the other hand, it appears to be the increase of carbonic anhydride in the muscular substance which excites the sensory nerves of muscle, and so reflexly influences the respiratory mechanism.

The question of dyspnoëa due to work is discussed at length; other subjects treated are Cheyne-Stokes respirations, and the very similar periodicity of respiratory activity occurring in morphine poisoning.

The blood gases and respiratory activity appear to bear no constant relationship to each other; thus the animal may breathe when the arterial blood has much oxygen and little carbonic anhydride, and the pauses may occur when the opposite condition of the blood gases is present. Fatigue of the respiratory centre is also dismissed as an explanation of the phenomena; the real explanation is left an unsettled problem.

W. D. H.

Action of Salts on the Gastric Digestion of Fibrin, and of Acids on the Saline Digestion of Fibrin. By A. DASTRE (*Compt. rend. Soc. Biol.*, 1894, 778—779; compare *Abstr.*, 1895, ii, 300).—The proteolytic action of acidified pepsin is prevented by concentrated salts like sodium or ammonium chloride: the proteolytic action of concentrated saline solutions is prevented by acidification.

W. D. H.

Oxidising Power of the Blood. By J. E. ABELOUS and G. BIARNÈS (*Compt. rend. Soc. Biol.*, 1894, 536—538, 799—801).—Salicylaldehyde is not oxidised to salicylic acid by the air, or by distilled water, or physiological saline solution at 37°. The acid is, however, formed when defibrinated blood or serum is added at this temperature, although this does not occur at the temperature of the air. The amount of oxidation varies with the blood of different animals, and is attributed to a specific ferment, which is destroyed by boiling. Certain organs (testis, thyroid, adrenals, thymus, kidney, liver, lung, and spleen) possess the same power, which is lost when vitality is destroyed; it is not shown by muscles, brain, or pancreas.

W. D. H.

Action of Blood-serum on Glycogen and on Maltose. By ÉMILE E. BOURQUELOT and EUGÈNE GLEY (*Compt. rend. Soc. Biol.*, 1895, 247—250).—Blood serum has a saccharifying action on glycogen, the action being more energetic than that of saliva; the sugar formed is not, however, maltose but dextrose.

W. D. H.

Formation of Glycogen in the Animal Organism. By MAURICE KAUFMANN (*Compt. rend. Soc. Biol.*, 1895, 277—280), and by A. DASTRE (*ibid.*, 280—283).—The first paper discusses the origin of glycogen: the author believes that in man and the higher animals, it originates solely in the liver, and that the glycogen in the blood and elsewhere is derived from the liver, and not formed in the cells where it can be detected.

The second paper discusses the same question with the opposite conclusion, maintaining the doctrine that glycogen is fixed, not circulating.

W. D. H.

Glycogen in Lymph. By A. DASTRE (*Compt. rend. Soc. Biol.*, 1895, 242—247).—Lymph contains 0.097 part of glycogen per 1000. After 24 hours, it is destroyed in the lymph by a diastatic ferment. Glycogen is present in the cells, but not in the plasma.

W. D. H.

Thyreo-antitoxin. By SIGMUND FRÄNKEL (*Wiener med. Blätter*, 1895, No. 48).—After removal of proteid and gelatinous matter from thyroid extract, the physiological substance which possesses curative powers remains unprecipitated, and so far as experiments have gone as yet, is identical with a substance of the formula $C_6H_{11}N_3O_5$, called provisionally, *thyreo-antitoxin*, which can be crystallised out by concentration; it is very hygroscopic. It produces rapidity of pulse, but no fall of blood pressure, and when administered to animals deprived of their thyroids it delays the onset of death, and abolishes the nervous symptoms; it does not, however, prevent death.

W. D. H.

Uropoietic Diastase. By CH. RICHET (*Compt. rend. Soc. Biol.*, 1894, 525—528).—The alcoholic precipitate of extract of liver contains two ferments, the activity of which is destroyed by boiling; when added to liver extracts, the changes produced are a diminution of glycogen, and an increase of urea.

W. D. H.

Composition of the Milk of Various Animals. By AUGUSTO PIZZI (*Staz. Sper. Agrar.*, 1894, **26**, 615—639).—The volatile, fatty acids of milk from various sources, and the points of fusion and solidification of the butter were determined with the following results.

	Woolly number.	M. p. of butter.	Solidification of butter.
Woman	1.42	32.0°	22.5°
Goat	28.60	36.5	31.0
Sheep	32.89	29.0	12.0
Buffalo	26.18	38.0	29.0
Sow	1.65	28.0	12.0

The Woolly numbers are also given for the following butters: Mare's, 11.22; ass, 13.09; rabbit, 16.06; bitch, 1.21; cat, 4.40; and rat, 2.97. The odour, colour, and taste, &c., of the butter are described.

The following percentage results were obtained with the milk of (1) sheep, (2) goats from the Appenines, (3) buffalos, and (4) rabbits.

	Sp. gr. at 15°.	Water.	Fat.	Albumin and casein.	Lactose.	Ash.
1.	1.0413	80.425	9.66	4.44	4.37	1.10
2.	1.0326	86.75	5.35	3.64	3.60	0.66
3.	1.0332	82.20	7.95	4.13	4.75	0.97
4.	1.0493	69.50	10.45	15.54	1.95	2.56

Determinations of volatile fatty acids in the colostrum obtained from cows at successive periods, showed increased amounts as the conversion into normal milk proceeds. N. H. J. M.

Sterilisation of Milk and the Lactic Fermentation. By PAUL CAZENEUVE (*Bull. Soc. Chim.*, 1895, [3], **13**, 502—509).—The milk is sterilised by heating it in boiling water in screw-stoppered bottles, which are capsuled with tin, and completely immersed in the water, the air escaping through capillary orifices in the capsules subsequently closed by compression. As the bottles cool, the capsules and necks are coated with solid paraffin to eliminate all possibility of the entrance of air.

Of the various samples of milk subjected to this treatment, some fresh, some about to turn sour, and some actually putrescent, none underwent further change—even when kept for days at 35°. The lactic ferment seems to be attenuated and, to a large extent, destroyed by the process, for the sterilised samples remained for the most part unchanged after the admission of sterilised air, and did not give rise to colonies when sown in a gelatin medium.

Milk thus treated is stated to be more digestible than new milk, and has not the objectionable colour or taste of milk boiled in an open vessel, or that sterilised at higher temperatures. The process has been tried on the commercial scale. JN. W.

Proteids of Normal Urine. By KARL A. H. MÖRNER (*Skand. Archiv Physiol.*, 1895, 332—437).—Although healthy human urine for

practical purposes contains no proteïd, yet there is proteïd matter present in extremely small quantities. For the purpose of ascertaining its nature, each experiment required many litres, often 80 or 90 litres of urine. This proteïd or proteïd-like material is contained partly in suspension in the ordinary mucous cloud or nubecula, and partly in solution. The research naturally, therefore, divides itself into two parts. The conclusions drawn in reference to the nubecula are the following.

The sediment of normal urine contains a specific member of the mucin group, named *urine-mucoid*, which probably originates from the mucous membrane of the urinary passages. It has the percentage composition: C, 49·4, N, 12·74, S, 2·3, and is readily soluble in ammonia. From its solutions, it is precipitable by acetic and other acids, and is only slightly soluble in excess of the acid. Its solution is lævorotatory ($\alpha_D = -62-67^\circ$), and it reduces alkaline copper solution slightly; after boiling with hydrochloric acid, however, it is strongly reducing. It gives the proteïd colour-reactions. With α -naphthol and concentrated sulphuric acid, it gives no carbohydrate reactions. It contains neither phosphorus (nucleic acid) nor conjugated sulphuric acid (chondroitin-sulphuric acid). In many particulars it agrees with the ovomucoid of eggs.

The soluble proteïd in urine is chiefly serum-albumin; but some is precipitable by acetic acid; and this part consists of a nucleo-proteïd. Precipitated with the proteïd, chondroitin-sulphuric acid is constantly present; this is considered to originate in the kidneys where its presence has been previously shown. The relative amounts of albumin and this acid are variable; thus there is no compound between them. In some cases, taurocholic acid is present in small quantities.

W. D. H.

Excretion of Creatinine during Regular Work on a Mixed Diet. By EDWIN ACKERMANN (*Compt. rend. Soc. Biol.*, 1894, 659—660).—The experiments made on a man on a mixed diet, and doing regular work, show that, in the mean, the daily output of creatinine is 1·254 gram or 0·017 gram per kilo. of body weight. The amount is lessened by rest.

W. D. H.

Resistance of Invertin to Heat. By ROUSSY (*Compt. rend. Soc. Biol.*, 1895, 400—402).—The fever-producing property of invertin is not destroyed by temperatures between 100° and 150° , although it is lessened. The diastatic property of the same substance also is simply attenuated, and not completely destroyed by the same temperatures.

W. D. H.

Chemistry of Vegetable Physiology and Agriculture.

Mannitol Fermentation in Sicilian Wines. By G. BASILE (*Staz. Sper. Agrar.*, 1894, **26**, 451—497).—Sicilian wines are subject to an abnormal fermentation, which, in some years, causes very great

loss, the chief product of this fermentation being mannitol produced from the glucose; it is generally the red wines which are attacked rather than the white wines, and it is chiefly in hot, dry seasons that this fermentation prevails. The bacterium ferment which produces mannitol, shows the Brownian motions when anaërobic, but is inert when aërobic; and although it may coexist with the alcoholic ferment, it does not predominate until the alcoholic ferment loses its activity. The action of the mannitol ferment may be hindered by racking off the wine when the glucose has been entirely consumed by the alcoholic ferment; or the wine may be pasteurised, and resown with the alcoholic ferment.

N. H. J. M.

Action of Metallic Salts on the Lactic Fermentation. By ALLYRE CHASSEVANT (*Compt. rend. Soc. Biol.*, 1895, 140—142; compare *Abstr.*, 1894, ii, 63).—Salts of magnesium, sodium, lead, gold, and copper, when added to milk in small quantities, produce an acceleration of the lactic fermentation, especially at the commencement. With gold and copper this, in time, is converted into a hindering action. Mixtures of the salts produce a similar action.

W. D. H.

Chemistry of the Barley Plant. By CHARLES F. CROSS, EDWARD J. BEVAN, and CLAUD SMITH (*Ber.*, 1895, 28, 2604—2609).—The plants were grown during 1894—95 on two of the plots at the Royal Agricultural Society's experimental station at Woburn, one plot being regularly manured, the other left entirely without manure. Samples of the plants were gathered at various periods and analysed, the dried residue, permanent fibre, and the furfuraldehyde obtained from both the dried residue and the permanent fibre being estimated. The results show that the difference in the treatment of the two soils has only a slight influence on the composition of the plant. The atmospheric conditions affect the results very materially, especially the amount of permanent fibre. In the comparatively wet season of 1894 this increased in quantity throughout the whole period, whilst in 1895, the sunny spring of which was followed by wet weather, the amount of permanent fibre became less after the middle of July, and again diminished towards the end of August. The furfuroids appear to be accumulated as the growth of the plant proceeds, chiefly in the stable or cellulose-like form; at the same time, as shown by the diminution which occurred during the last period of 1895, they are able, when required, to contribute to the necessities of the plant during ripening.

A. H.

Tannin Colouring Matters of Red Grapes. By L. SOSTEGNI (*Staz. Sper. Agrar.*, 1894, 27, 400—413).—The red colouring matter obtained by concentrating wine on a water bath, adding hydrochloric acid, and allowing the mixture to remain overnight, was separated into two portions—one soluble in alcohol, the other insoluble. The former contained C = 56.62, H = 5.00 per cent., the latter C = 57.62, H = 4.70 per cent. The reactions of the two portions, which are fully described, indicate the presence in both of catechol and

phloroglucinol. The soluble substance seems to contain some other aromatic compound.

More colouring matter was obtained from the residue left on distilling the alcoholic extract of the marc of grapes; after precipitation by water, the substance was washed with hot water, treated with ether, redissolved in alcohol and again precipitated. The reactions much resembled those of the other two products. When heated with sulphuric acid (15 per cent.) at 130° for 12 hours, a compound containing rather more hydrogen than those mentioned above was obtained (C = 55.77 and 55.88; H = 6.30 and 6.18 per cent.). The results generally point to the presence of catechol and resorcinol, possibly also of quinol.

N. H. J. M.

Analytical Chemistry.

Arrangement for Washing Precipitates with Boiling Water.

By FRANK F. JEWETT (*J. Amer. Chem. Soc.*, 1895, **17**, 517—518).—The water is boiled in a wash-bottle fitted with a trebly perforated indiarubber cork, the steam escaping through an open clip. When a precipitate has to be washed, the clip is closed, and the pressure of the steam at once drives the water through a tube bent at right angles, connected by a few inches of rubber tubing to a jet, which is wound about with a strip of non-conducting material, and may, therefore, be easily handled. The bottle is also connected with an inverted flask fitted with a tube to allow escape of air. If the pressure should become too great, the steam simply forces the boiling water into the inverted flask. On reopening the clip, the water immediately returns to the lower flask.

L. DE K.

Estimation of Perchlorate. By D. ALBERT KREIDER (*Zeit. anorg. Chem.*, 1895, **10**, 277—288, and *Amer. J. Sci.*, 1895, [3], **50**, 287—297).—Potassium perchlorate, when boiled with potassium iodide and phosphoric acid, is not reduced until the temperature reaches 215—220°, at which temperature metaphosphoric acid is formed; if, however, metaphosphoric acid is employed, reduction takes place at 200°, and the author has attempted to employ this reaction for the estimation of perchlorate. The best results are obtained by gradually adding the potassium iodide to the mixture heated at about 300° in a current of carbonic anhydride, but the error amounts to from 2 to 5 per cent. A number of experiments are described in which the perchlorate is melted with potassium iodide and an indifferent compound, and the metaphosphoric acid allowed to act on the mixture, but in no case could accurate results be obtained.

When potassium perchlorate is fused with aluminium sodium chloride, $\text{Al}_2\text{Cl}_6 \cdot 2\text{NaCl}$, chlorine is liberated, which is estimated by absorption in potassium iodide; the reaction must take place in an atmosphere of carbonic anhydride. The results obtained are, however, only accurate to from 1 to 5 per cent.

An accurate estimation of perchlorate is effected by estimating the oxygen evolved when the salt is heated at 400° ; this is effected by treating the gas with concentrated hydriodic acid in the presence of a slight excess of nitric oxide, the liberated iodine being titrated with a decinormal solution of arsenious acid. A full description of the apparatus employed is contained in the original paper; great care must be taken to exclude air, and this is effected by means of carbonic anhydride. In order to insure a steady evolution of oxygen from the perchlorate, the latter is covered with a layer of sodium potassium carbonate, the gas being collected in a suitable flask, and then gradually introduced into a flask containing a known quantity of concentrated hydriodic acid containing nitric oxide; meanwhile great care must be taken to shake the mixture without intermission, as otherwise higher oxides of nitrogen will be formed. A constant error of $+0.0003$ gram of potassium perchlorate must be allowed for, but otherwise the results are accurate. If other oxidising compounds besides perchlorate are present, they are reduced by a reagent which is indifferent to perchlorate, and the filtered solution then evaporated to dryness, and the residue treated as above. The method is also applicable to the estimation of oxygen in air, and in all cases where oxygen is evolved.

E. C. R.

Qualitative Analysis of Mixtures of Sulphites, Carbonates, and Sulphates. By LEOPOLDO GIACOMELLI (*L'Orosi*, 1895, 18, 155).—The saline mixture is placed in a small flask furnished with a tap-funnel and delivery tube, and the sulphurous and carbonic anhydrides, expelled by the gradual addition of, and finally boiling with, dilute hydrochloric acid, are passed through a solution of potassium chromate containing potash free from sulphates and carbonates. If, at the end of the operation, the acid liquid is turbid with sulphur, the mixture must have contained a thiosulphate, whilst, if sulphates are present, these must have been present as such in the original solution. The presence of sulphates in the chromate solution, after warming and acidifying with dilute hydrochloric acid, points, on the other hand, to that of sulphites in the original substance, provided no thiosulphate was present, whilst an effervescence on adding the acid to the chromate solution can only be due to the decomposition of alkali carbonate.

JN. W.

Reduction of Selenious and Selenic acids by Hydriodic acid. By FRANK A. GOOCH and W. G. REYNOLDS (*Zeit. anorg. Chem.*, 1895, 10, 248—252; and *Amer. J. Sci.*, 1895, [3], 50, 249—252).—Muthmann and Schäfer's method (*Abstr.*, 1893, ii, 318) of estimating selenious acid by reducing it with hydriodic acid and titrating the liberated iodine with thiosulphate is not accurate except under special conditions, but accurate results can be obtained if the iodine is removed from the sphere of action as it is liberated. The mixture of selenious acid, potassium iodide, and hydrochloric acid is distilled, and the iodine collected in a Will-Vareuttrapp absorption apparatus; a small quantity of iodine, however, always remains in the distillation flask, and this must also be titrated with thiosulphate. Not more than 0.2 gram of selenium dioxide is used for each estimation, and 3 grams

of potassium iodide dissolved in 100 c.c. of water; a large excess of hydrochloric acid is without influence on the reaction. Selenic acid is reduced by potassium iodide and hydrochloric acid much more slowly than selenious acid, and the reaction takes place quantitatively only in the presence of a large excess of hydrochloric acid. By employing the distillation method, accurate results are obtained.

E. C. R.

Reduction of Selenic acid by Hydrochloric acid. By FRANK A. GOOCH and P. S. EVANS, jun. (*Zeit. anorg. Chem.*, 1895, **10**, 253—255, and *Amer. J. Sci.*, 1895, [3], **50**, 400—402).—Selenic acid is completely reduced to selenious acid by heating with hydrochloric acid under certain conditions; chlorine is liberated, and can be estimated by means of potassium iodide and thiosulphate. The concentration of the hydrochloric acid is very important; with a solution containing less than 10 per cent. by volume of hydrochloric acid of sp. gr. = 1.2, no action takes place after five minutes' heating. Accurate results are obtained by employing a solution containing one-third of its volume of hydrochloric acid of sp. gr. 1.2, and continuing the distillation until one-third of the total volume in the distillation flask has passed over. Not more than 0.2 gram of selenic acid must be used for each determination. If the strength of the hydrochloric acid is allowed to reach 50 per cent., selenium comes over in the distillate.

E. C. R.

Reduction of Selenic acid by Potassium Bromide in Acid Solution. By FRANK A. GOOCH and W. S. SCOVILLE (*Zeit. anorg. Chem.*, 1895, **10**, 256—258, and *Amer. J. Sci.*, 1895, [3], **50**, 402—404).—Selenic acid is reduced to selenious acid by distillation with potassium bromide and sulphuric acid, the completeness of the action depending on the amount of potassium bromide employed, the strength of the sulphuric acid, and the concentration of the solution during the distillation. When the distillation is continued too long, selenium is liberated, and if an excess of potassium bromide is used, it is difficult to remove the liberated bromine from the distillation flask before the reduction to selenium takes place. The best results are obtained by employing 0.25 gram of selenic acid, 20 c.c. of dilute sulphuric acid (1 : 1), 1 gram of potassium bromide, and a total volume of 60 c.c.; the distillation is carried on until the reduction to selenium commences, which is usually the case when the solution in the distillation flask measures about 35 c.c. The bromine in the distillate is estimated in the usual manner.

E. C. R.

Estimation of Nitrogen in Fertilisers containing Nitrates. By H. C. SHERMAN (*J. Amer. Chem. Soc.*, 1895, **17**, 567—576).—After studying the various methods for the estimation of nitrogen in manures containing nitrates, the author arrives at the following conclusions. The official (American) methods are perfectly trustworthy if the directions are followed closely and the digestion with acid is continued for a short time after the mixture has become practically colourless. In analysing samples containing a considerable amount of chlorides, it is, however, advisable to use zinc-dust and to cool the acid mixture before adding it to the sample. It is best to

digest for some time at the ordinary temperature before adding the zinc. If the amount of nitric nitrogen is very large, the boiling must be continued a long time, or else a little permanganate must be added to complete the action. L. DE K.

Estimation of Small Quantities of Phosphoric acid by the Citrate Method. By E. G. RUNYAN and HARVEY W. WILEY (*J. Amer. Chem. Soc.*, 1895, **17**, 513—514).—When the amount of phosphoric acid is below 10 per cent., the very convenient and accurate citrate process fails to give results corresponding with those obtained by the molybdate method.

The authors now advise adding a known amount of phosphoric acid, for instance, a solution of calcium phosphate of known strength, in order to bring the strength of the sample up to between 15 and 30 per cent. The results, after allowing, of course, for the added phosphoric acid, will then be quite trustworthy. L. DE K.

Some Conditions affecting the accuracy of the Estimation of Potash as Potassium Platinochloride. By A. L. WINTON (*J. Amer. Chem. Soc.*, 1895, **17**, 453—466).—The author has investigated the conditions under which potassium platinochloride is obtained, and has tabulated the results.

The most interesting result, from an analytical point of view, is that the precipitate obtained by adding platinic chloride to a concentrated solution of a potassium salt consists chiefly of radiating crystals, a characteristic form having six arms, formed by the intersection at right angles of three bars. Numerous globular cavities in the crystals show that, during their rapid formation, mother liquor is inclosed; the compound is therefore difficult to free from water, retaining some even at 160°. On the other hand, the compound formed by mixing dilute solutions of the two metals, and then evaporating, crystallises in octahedrons, generally attached to one another, forming crystalline plates; these crystals are comparatively free from cavities, and become very nearly anhydrous after drying for three hours at 100°.

L. DE K.

Estimation of Lime in Soil. By G. BASILE and E. DE CELLIS (*Staz. Sper. Agrar.*, 1894, **27**, 115—156).—In determining the amount of lime in soil, the magnesium carbonate should also be estimated and the physical condition of the carbonates examined; the nature of the predominating rocks of the surrounding country may have to be taken into account in forming an opinion as to the availability of the lime. Calcimetry should be employed in conjunction with direct estimation of lime and of magnesia if present. The error in the calcimetric method increases with soils rich in lime.

Carbonic anhydride is best determined by weighing, employing Schrötter's or a similar apparatus. For calcimetry, Scheibler's apparatus is the best; Bernard's method is not recommended, but that of Houdaille and Sémichon deserves attention. N. H. J. M.

Volumetric Estimation of Zinc, and a New Indicator for Ferrocyanides. By GEORGE C. STONE (*J. Amer. Chem. Soc.*, 1895, **17**, 473—477).—The thoroughly oxidised solution of the ore is

washed into a 500 c.c. flask, and barium carbonate, suspended in water, is added until the precipitate of iron and aluminium hydroxides rapidly settle. After making up to the mark, the liquid is filtered, and aliquot portions are taken for titration. The author prefers titrating the manganese only, by means of the well-known permanganate method; the joint amount of zinc and manganese is titrated by means of potassium ferrocyanide.

It was found necessary to obtain a suitable indicator, as both copper sulphate and uranium acetate act on the manganous ferrocyanide; ferric chloride was also quite unsuitable. A very weak solution of cobalt nitrate is free from this objection; it must be applied as follows: A drop of it is placed on a white porcelain plate and a drop of the solution under treatment is added so that the drops touch but do not mix. The slightest excess of ferrocyanide is indicated by a faint greenish zone.

L. DE K.

Volumetric Estimation of Copper. By MATTEO SPICA (*Staz. Sper. Agrar.*, 1894, **26**, 593—600).—The copper solution is titrated with a solution of potassium ferrocyanide (containing $K_4FeCy_6 + 3aq = 0.0845691$ per cent.), paper prepared with ferric chloride being employed as indicator. The method gave results agreeing well with those obtained by the electrolytic process, whilst Bornträger's method (*Abstr.*, 1894, ii, 120) was found to be unsatisfactory.

The presence of nickel does not greatly affect the result if the quantity is small; but any error from this source may be avoided by first precipitating the copper as sulphide, dissolving the latter in a little nitric acid, treating with ammonia and titrating. This process has the further advantage of rendering it unnecessary to precipitate the iron with ammonia. A table of results obtained by the new method is given.

N. H. J. M.

Qualitative Separation of the Metals of the Iron Group. By C. L. HARE (*J. Amer. Chem. Soc.*, 1895, **17**, 537—539).—The solution is mixed with ammonium chloride, and precipitated with excess of ammonia; after warming and filtering, the precipitate is boiled with aqueous soda, in which the alumina dissolves, and may be identified by acidifying and reprecipitating with ammonia. The insoluble residue is again boiled with soda, adding a few c.c. of hydrogen peroxide; a yellow solution indicates chromium, this is acidified with acetic acid, and the presence of chromium confirmed by means of lead acetate. The insoluble residue is finally tested for iron by the ferrocyanide test.

The ammoniacal solution is mixed with ammonium sulphide (free from polysulphide), warmed, and filtered, and the precipitate formed is treated with cold, dilute, hydrochloric acid to dissolve manganese and zinc, which are separated as usual; the insoluble residue is then dissolved in nitro-hydrochloric acid, and after expelling the excess of the latter by heating, tartaric acid is added, and then a large excess of aqueous soda. From this solution the cobalt is precipitated by a current of hydrogen sulphide, and the precipitate may be further

recognised by the borax bead test. On acidifying the alkaline solution, nickel sulphide separates, and may then also be tested with borax.

L. DE K.

Qualitative Separation of Chromium from Iron. By LEOPOLDO GIACOMELLI (*L'Orosi*, 1895, 18, 48—49).—The methods usually employed in the separation of chromium from iron in systematic qualitative analysis, yield unsatisfactory results when the relative amount of chromium is small, as the salts of the latter are liable to be carried down with the ferric hydroxide, or retained by the ferric oxide. The chromium is best separated by oxidising the ammonia precipitate containing only the mixed ferric, chromium, and aluminium hydroxides with a few drops of nitric acid, and a crystal or two of potassium chlorate; the precipitate should be fairly well dried in a capsule before the addition of the oxidising agent, and the heating with the latter continued until the evolution of chlorinous fumes ceases. The chromium being thus oxidised to chromic acid, the iron and alumina can be precipitated as hydroxides with ammonia from the aqueous solution, and separated by means of caustic soda in the usual way, whilst the chromic acid can be recognised in the filtrate by means of lead acetate after acidification with acetic acid.

JN. W.

Estimation of Benzene in Illuminating Gas. By WILLIAM A. NOYES and W. N. BLINKS (*J. Amer. Chem. Soc.*, 1894, 16, 697—698).—One hundred c.c. of gas is measured in a Bunte burette, best with a side tube or bottle attached below, so that the gas is brought to atmospheric pressure. The water is then completely removed from the cup above, and the water in the burette is driven down to the lower stopcock as usual, for the introduction of reagents. Two or three c.c. of absolute alcohol is poured into the cup, and allowed to enter the burette 1 c.c. at a time, care being taken that the walls of the burette are thoroughly moistened with it. After withdrawing the alcohol in the usual manner, 2 or 3 c.c. of water is admitted above and withdrawn below, and more water is then admitted until the gas is brought to the original pressure. The difference between the two readings represents the benzene vapour which has been absorbed by the alcohol.

L. DE K.

Densimetric Estimation of *d*-Glucose in Urine. By THEODOR LOHNSTEIN (*Pflüger's Archiv*, 1895, 62, 82—110).—The multiplicator in Roberts' method of sugar estimation is not a constant, but varies with the specific gravity of urine free from sugar, with the percentage of sugar, and with the temperature. The removal of the yeast also makes a difference.

If p = amount of sugar,
 t = temperature at which the sp. gr. is taken,
 S' = sp. gr. of urine free from sugar,
 p = percentage volume,
 f = Robert's factor,

and the yeast remain in suspension.

$$f = 234 - \frac{3}{7}(p - 3) + \frac{3}{4}(t - 20) + 487 S' - 1.02$$

From this equation it follows that if p varies from 0 to 10, t from 15° to 25° , and s from 1.01 to 1.03, f will vary from 222.3 to 244. There is thus a possible error of 5 per cent., although for most average cases the number 234 is pretty near.

If S_1 = sp. gr. of the urine + yeast before fermentation,

S_2 = " " " " after " "
 t_1 and t_2 = the respective temperatures at which S_1 and S_2
 are observed.

v_1 = volume of original urine.

v_2 = " " urine after the addition of yeast,

then $p = [S_1 - S_2 + 0.002(t_1 - t_2)] \times 234$ if t_2 lies between
 15° and 20° ,

and $= [S_1 - S_2 + 0.003(t_1 - t_2)] \times 234$ if t_2 lies between
 20° and 25° .

also $S_1 = S_2 + \frac{S_1 - S_2}{6}$.

A better value for p is the following.

$$p = \frac{v_2}{v_1} (S_1 - S_2 + \left\{ \begin{array}{l} 0.0002(t_1 - t_2) \\ 0.0003(t_1 - t_2) \end{array} \right\} f).$$

S_1 and S_2 should be known to three decimal places.

By such equations, the percentage of sugar can be estimated to
 0.1 per cent. W. D. H.

The Polarising Microscope and Zeiss' Refractometer applied to Butter Analysis. By CARLO BESANA (*Staz. Sper. Agrar.*, 1894, 26, 601—604).—By means of the polarising microscope, 5 per cent. of margarine in butter can be detected; but butter which has been melted, and old butter, give rise to an appearance similar to that caused by margarine, so that the method can only be utilised for establishing the purity of butter.

As regards Zeiss' refractometer, determinations should be made at a definite temperature (35° is convenient), as rise of temperature lowers the refractive indices; the temperature should be maintained constant during the experiment by means of a current of water. One hundred and eight samples of butter gave at this temperature the average result = 46, the maximum and minimum limits being respectively 47 and 44.8. Commercial margarine showed from 50 to 51; cocoa fat, 38.2; olive oil, 57; and sesame oil, 62. No effect on the result seemed to be caused by the butter being rancid. Considering the comparatively slight differences in the refractive indices of butter and margarine, a considerable admixture of the latter has but little effect on the result. Samples of butter which give results lower than 46 may be considered genuine; in others, the volatile acids should be determined.

N. H. J. M.

Estimation of Volatile and Insoluble acids in Butter. By W. H. BEAL (*J. Amer. Chem. Soc.*, 1894, 16, 673—676).—2.5 grams

of the clear butter fat is introduced into a long, narrow, 200 c.c. Erlenmeyer flask. Saponification is accomplished by adding 2 c.c. of aqueous potash (1—2), and 5 c.c. of 95 per cent. alcohol and boiling, using a reflux condenser; five minutes is amply sufficient. The spirit must then be removed by means of a filter pump (Nilson, *Abstr.*, 1889, 801). The soap is dissolved in 30 c.c. of hot water, and decomposed with 20 c.c. of 20 per cent. phosphoric acid; the volatile acids are then driven off in a current of steam generated by boiling about 700 c.c. of water in a litre flask, but in order to prevent accumulation of liquid in the Erlenmeyer flask, the contents of the latter should be kept boiling by means of a spirit lamp. The cooling apparatus consists of a deep trough, through which pass one or more glass spirals, fitted by india-rubber corks, and the distillate is collected in a wide-mouth Erlenmeyer flask, marked at 500 c.c., and carrying a funnel with a small filter. The distillate is finally titrated, as usual, with N/10 soda and phenolphthalein. When the distillate amounts to 500 c.c., it may be taken for granted that all the volatile acids have passed over, but by way of extra precaution another 50 c.c. may be distilled off and titrated separately. To collect the insoluble acids, the condenser and connections are rinsed back with boiling water into the distilling flask; after cooling, the acid liquid is filtered through the same filter, and the washing and cooling is repeated until all the phosphoric acid is removed. The filter is then extracted with boiling alcohol, which is allowed to run into the distilling flask. After expelling the alcohol and drying the fatty acids at 100°, they are weighed.

L. DE K.

Untrustworthiness of Creamometers for the Estimation of Fat in Pasteurised Milk. By PAUL CAZENEUVE and E. HADDON (*Bull. Soc. Chim.*, 1895, [3], 13, 500—502).—It is generally admitted that the cream in boiled milk cannot be accurately estimated by means of the creamometer, but no exact experiments seem to have been made on this point, nor any with milk sterilised by the well-known methods.

The authors find that milk sterilised by Pasteur's method at 70—75°, or 80°, yields, at most, half its cream, even after 27 hours, but that, when sterilised at 100° or 115° by Cazeuueve's method (this vol., ii, 120), out of contact with the air, it yields practically the whole of its cream in the usual way.

The boiling of milk in the open air probably causes the oxidation and partial coagulation of the casein, and so leads to the retention of the fat.

JN. W.

Estimation of Urea in Blood and Tissues. By MAURICE KAUFMANN (*Compt. rend. Soc. Biol.*, 1895, 145—147).—Gréhan's method of estimating urea consists in extracting the blood or tissues with alcohol, evaporating the alcoholic extract, and decomposing the urea in the residue with Millon's reagent ("mercure nitreux") into equal volumes of carbonic anhydride and nitrogen in the vacuum of a mercurial pump. Other extractives are not thus broken up. The results are described as very satisfactory.

W. D. H.

Estimation of Urea in Animal Organs and Liquids. By BERNHARD SCHÖNDORFF (*Pflüger's Archiv*, 1895, **62**, 1—57).—After a review of previous work on the subject of the estimation of urea, experiments are recorded which led to the following conclusions. The amido-acids, glycocine, alanine, leucine, sarcosine, taurine, tyrosine, metamidobenzoic acid, and aspartic acid give off all their nitrogen when treated by the Kjeldahl process. They are not precipitated by a mixture of phosphotungstic and hydrochloric acids; when heated with phosphoric anhydride at 150° , they do not give off nitrogen; at 230° , however, they give off all their nitrogen, except taurine, for which a temperature of 240° is necessary; and when heated with an alkaline solution of barium chloride at 150° , only traces of carbonic anhydride, coming within the limits of experimental error, are evolved.

Urea is completely decomposed into carbonic acid and ammonia by four and a half hours' heating at 150° . By heating with phosphoric anhydride at 150° , it yields all its nitrogen; by heating at 150° with alkaline solution of barium chloride in a sealed tube, the full amount of carbonic anhydride is obtained.

The substances of the uric acid group (uric acid, allantoïn, allantoxantine, caffeine, xanthine, guanine) are insoluble in absolute alcohol, and are, with the exception of allantoïn and allantoxantine, completely precipitated from their solutions by the mixture of phosphotungstic and hydrochloric acids.

Creatine is almost insoluble in absolute alcohol, and is not precipitated by the acid mixture (see below). On heating a solution for ten hours with dilute acetic acid, it is converted into creatinine, and is then precipitable by the acid mixture to the extent of 74 per cent. By heating with phosphoric anhydride at 150° , it yields 1 mol. of ammonia, splitting up into methylhydantoïn and ammonia. By heating with alkaline barium chloride solution, it splits up into sarcosine and urea, so that, therefore, on analysis, 1 mol. of carbonic anhydride and 2 mols. of ammonia are obtained. By heating with phosphoric anhydride at 150° , creatine yields 1 mol. of ammonia, and with alkaline barium chloride solution at 150° , 1 mol. of carbonic anhydride, whilst urea under the same circumstances yields 2 mols. of ammonia and 1 mol. of carbonic anhydride respectively. In estimating urea by this method, it is necessary that creatine should be absent.

Creatinine is completely precipitable from an aqueous solution by a mixture of phosphotungstic and hydrochloric acid. By heating with alkaline barium chloride solution at 150° , it behaves like creatine, but with phosphoric anhydride there is only an incomplete decomposition.

The method devised from such experiments for the estimation of urea in blood and other animal fluids is as follows: the proteïd and extractives are first precipitated by the acid mixture. In the case of organs, these are finely minced, and extracted with alcohol; the extract, after acidification with acetic acid, is evaporated to dryness at 50° , and the residue taken up with alcohol and again evaporated to dryness. The residue is then taken up with hot water, and the acid mixture added. In either case, the precipitate produced

filtered off, the filtrate made alkaline with powdered lime, and in it the total nitrogen, the nitrogen evolved by heating at 150° with phosphoric anhydride, and the carbonic anhydride obtained by heating with alkaline barium chloride solution at 150° are estimated, and the results compared; there should be 1 mol. of carbonic anhydride to 2 mols. of ammonia.

The acid mixture has the following composition: 100 c.c. of hydrochloric acid (sp. gr. 1.124), or an equivalent quantity of sulphuric acid, is placed in a litre flask, which is then filled up with phosphotungstic acid solution. W. D. H.

Detection of Creatinine in Urine. By WILLIAM OECHSNER DE CONINCK (*Compt. rend. Soc. Biol.*, 1895, 111—112).—The coloration produced in pathological urine by the addition of sodium nitroprusside and sodium hydroxide may be due not only to creatinine but also to acetone. W. D. H.

Morphine Reactions. By GUSTAVE BRUYLANTS (*Bull. Soc. Chim.*, 1895, [3], 13, 497—500).—In addition to the well-known violet coloration with sulphomolybdic acid, a green coloration may be produced by varying the conditions of reaction. In either case, the alkaloïd is dissolved in concentrated sulphuric acid; to obtain the violet coloration, a drop of the cold solution is mixed on a white tile with a drop of the reagent (0.01 gram of ammonium molybdate per c.c.), whilst, to obtain the green coloration, the morphine solution is previously heated for a few minutes on a water bath. Both colorations are changed to orange by the addition of a crystal of nitre.

Similar colour reactions are given by the other opium alkaloïds.

The iodic acid test may be modified by adding the solid acid to a solution of morphine in concentrated sulphuric acid at 100° ; a lilac coloration is formed, changing to red and slowly disappearing; or, with larger quantities of iodic acid, a red coloration is produced at once. JN. W.

Estimation of Albumin in Cow's Milk. By L. L. VAN SLYKE (*J. Amer. Chem. Soc.*, 1894, 16, 712—715).—*Estimation of Casein.*—Ten grams of milk is diluted with 90 c.c. of water at 40 – 42° , mixed with 1.5 c.c. of 10 per cent. acetic acid, and the mixture stirred with a glass rod and allowed to remain for about five minutes. The coagulated casein having been first washed by decantation, and then a few times on a filter, the filter and contents are treated for nitrogen by the Kjeldahl process. The author uses the factor 6.25 for the calculation of the nitrogen to casein.

Estimation of Albumin.—The filtrate from the casein is placed in a boiling water bath for 10 or 15 minutes. The precipitate, after washing, is then also treated by Kjeldahl's method. The same factor is used.

Remaining Nitrogenous Compounds.—The author prefers to take these by difference, by subtracting from the amount of total nitrogen compounds (determined by Kjeldahl's method) the sum of the casein and albumin. L. DE K.

General and Physical Chemistry.

Refractometric Observations. By JAN F. EIJKMAN (*Rec. Trav. Chim.*, 1895, **14**, 185—202; compare *Abstr.*, 1894, ii, 173).—The author has determined the refractive indices for the hydrogen lines α and β and A of a large number of organic substances, each being examined at two temperatures differing by 30° to 125° .

At high temperatures, Gladstone and Dale's molecular refraction formula gives too low values, whilst Lorenz's expression gives too high values; it should therefore be possible to obtain a molecular refraction formula which should give concordant values at all temperatures. By calculating from the experimental numbers now obtained, the author finds that the results are best represented by the expression $(n^2 - 1)M/(n + 0.4)$, in which n is the refractive index, and M the molecular volume, and he therefore proposes to take this expression as the molecular refraction. If the new formula is employed, the agreement between the observed and calculated molecular refractions becomes very close, and the dispersion equivalent for the increment of an homologous series, CH_2 , acquires a constant value.

W. J. P.

Molecular Origin of the Absorption Bands of Salts of Cobalt and Chromium. By ALEXANDRE L. ÉTARD (*Compt. rend.*, 1895, **120**, 1057—1060).—Violet solutions of chromium sulphate and nitrate, and of chrome alum, exhibit a fine absorption band in the red, $\lambda = 678$ — 670 . Addition of a nitrite changes the colour of these solutions to lilac, and an arsenate turns them green, but the above characteristic band remains in the absorption spectrum, and is only shifted a little towards the red, $\lambda = 687$ — 680 . Chromic acid in concentrated solution also shows this band. On the other hand, anhydrous chromyl chloride, potassium chromate and dichromate, and roseochromic sulphate give no distinct band. The blue chromium potassium oxalate gives absorption bands in the red at $\lambda = 700$ — 693 and $\lambda = 732$ — 729 .

The red solution of cobalt sulphate gives a band, $\lambda = 654$ — 650 , and the red solution of cobalt chloride a band, $\lambda = 667$ — 642 . If these solutions are turned blue by heating and adding a little concentrated hydrochloric acid, two additional bands appear in the red, but the bands of the red solutions still remain visible.

The author concludes that the absorption bands of the chromium and cobalt compounds are not due to the atoms of the metals, but to the internal arrangement of the molecules. As these absorption spectra resemble in character those of the rare earth and of uranium compounds, the hypothesis that each band in the spectrum of a rare earth corresponds with some element, is not necessarily true.

H. C.

Anomalous Rotatory Dispersion of Malic acid. By RAFFAELE NASINI and G. GENNARI (*Gazzetta*, 1895, **25**, i, 417—438).—Employing a Landolt-Lippich polarimeter, fitted with the ray-filters recently

described by Landolt (Abstr., 1895, ii, 1), the authors have examined the rotatory dispersion of malic acid dissolved in various solvents, under different conditions of concentration and temperature; the mean wave-lengths, $\mu\mu$, in millionths of a millimetre of the various rays employed, are 665.9, 591.9, 553.0, 448.5, and 448.2. In a 4.6 per cent. aqueous solution at 20°, the specific rotation for all these rays is a lævo one; for red light of $\mu\mu = 665.9$, the value $[\alpha] = -1.87^\circ$, whilst for $\mu\mu = 448.2$ $[\alpha] = -2.51^\circ$; as the concentration increases, the temperature remaining the same, the solutions become more and more dextrorotatory, until in a 72.8 per cent. aqueous solution, the values of $[\alpha]$ for the above wave-lengths become $+1.80^\circ$ and $+6.39^\circ$ respectively. At intermediate concentrations, the solutions become inactive for one or other wave-length of light, although the particular solution for which $[\alpha] = 0$ for light of one wave-length is strongly active towards a different coloured light.

As the temperature of the solution rises, the value of $[\alpha]$ becomes more negative; thus at 7° a 33.24 per cent. aqueous solution has a specific rotation of $[\alpha] = +0.44^\circ$ for the ray $\mu\mu = 665.9$, and of $+2.63^\circ$ for the ray $\mu\mu = 448.2$, whilst at 41.5° these rotations become -5.96° and -5.84° respectively.

The addition of boric acid to the solution acts in the same way as a rise in temperature. Malic acid has nearly the same specific rotation in both methylic and ethylic alcohols, and the variation in rotation with varying concentration is of much the same kind as when water is the solvent; the solutions are, however, much more lævorotatory than aqueous solutions. The same seems to hold for propylic alcohol and acetone, although the lævorotation is not so high as when the solvent is methylic or ethylic alcohol.

A number of solutions of sodium malate were examined, showing that the specific rotations for light of various wave-lengths change in much the same way as with the acid itself. The dispersion coefficients of aqueous solutions of malic acid change very irregularly with the concentration, whilst those for sodium malate vary much less with the concentration.

After a full discussion of these anomalies, the authors are unable to furnish any explanation of them; they can hardly be due to changes in the degree of ionisation, malic acid being so slightly dissociated in aqueous solution. There is also no evidence indicating the existence of hydrates or polymerides in solution, as cryoscopic determinations show that, in concentrated aqueous solutions malic acid has the normal molecular weight.

W. J. P.

New Examples of the Superposing of the Optical Effects of Two Asymmetric Carbon Atoms. By PHILIPPE A. GUYE and C. GOUDET (*Compt. rend.*, 1895, 121, 827—829).—The amylic amylacetate of the formula $\text{CHMeEt}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{COO}\cdot\text{CH}_2\cdot\text{CHMeEt}$ contains two asymmetric carbon atoms, each of which should behave towards polarised light as though the rest of the molecule were inactive (Abstr., 1895, ii, 149). The authors have prepared compounds of the above formula from (a) a mixture of dextrorotatory amylacetic acid and racemic amylic alcohol, (b) a mixture of racemic amylacetic

acid and lævorotatory amylic alcohol, and (c) a mixture of the dextrorotatory acid and the lævorotatory alcohol. The first compound has the rotation $[\alpha]_D = +4.36$, and the second $[\alpha]_D = +1.54$. Theoretically, therefore, that of the third should be $+4.36 + 1.54 = +5.90$, and the number actually found was $[\alpha]_D = +5.64$, in close agreement with the theory.

The amylic amylmalonate, $\text{CHMeEt} \cdot \text{CH}_2 \cdot \text{CH}(\text{COO} \cdot \text{CH}_2 \cdot \text{CHMeEt})_2$, contains three asymmetric carbon atoms. Compounds of this formula were prepared from (a) dextrorotatory amylmalonic acid and racemic amylic alcohol, (b) racemic amylmalonic acid and lævorotatory amylic alcohol, and (c) dextrorotatory amylmalonic acid and lævorotatory amylic alcohol. The first compound has the rotation $[\alpha]_D = +6.10$, and the second $[\alpha]_D = +3.48$. The rotation of the third should therefore be $+9.58$, and the number actually found was $[\alpha]_D = +9.68$, the theory being thus again confirmed. H. C.

Optically Active Derivatives of Succinic acid. By PAUL WALDEN (*Zeit. physikal. Chem.*, 1895, **17**, 245—266).—The product of asymmetry, P, of a substance containing four groups of molecular weights g_1, g_2, g_3 , and g_4 attached to one asymmetric carbon atom, is obtained from the equation

$$P = \frac{(g_1 - g_2)(g_1 - g_3)(g_1 - g_4)(g_2 - g_3)(g_2 - g_4)(g_3 - g_4)(l \sin \alpha)^6}{(g_1 + g_2 + g_3 + g_4)^6};$$

omitting the constant term $(l \sin \alpha)^6$, the product of asymmetry is supposed by Guye and his supporters (*Abstr.*, 1893, ii, 561) to be a measure of the rotatory powers of optically active organic substances. The author has prepared a large number of derivatives of malic and succinic acids, and shows that in the several series of compounds thus obtained, the product of asymmetry does not, in most cases, even indicate correctly whether the specific rotation of a substance will increase or decrease when the mass g of one of the four groups is altered by substitution. Thus the specific rotations $[\alpha]_D$, and the molecular rotations $[M]_D$, of many of the substances mentioned in the accompanying table should be negative in sign, judging by the products of asymmetry, whilst others which should be either lævorotatory or inactive are highly dextrorotatory.

An inspection of the table shows that the ethereal salts of malic acid are dextrorotatory, the specific rotation rising as the mass of the alkyl group increases, until the maximum is attained at about the propylic salt; the amides are more lævorotatory than the salts, and their specific rotation increases with the mass of the substituted amidogen. The alkylic salts of the substituted malic acids are lævorotatory, and have about double the specific rotations of the parent alkylic malates; the derivatives of chlorosuccinic and bromosuccinic acids prepared from lævo-derivatives of malic acid are all highly dextrorotatory, and the specific rotations of the bromo-compounds are higher than those of the corresponding chloro-derivatives. Isomerides, or two compounds which contain groups of approximately the same mass, although of different kind, have not the same rotatory powers. Two substances of the same molecular weight, differ-

Substance.	[α] _D .	[M] _D .	<i>d</i> .	<i>n</i> .	R.	
					Observ.	Calc.
Dimethylic malate.....	- 6·85°	-11·10°	1·2317	1·4425	34·78	34·98
Diethylic "	-10·18	-19·35	1·1294	1·4362	44·00	44·18
Dipropylic "	-11·62	-25·32	1·0745	1·4380	53·26	53·40
Diisopropylic malate....	-10·41	-22·69	1·076	—	—	—
Diisobutyric "	-11·14	-27·39	1·0418	1·4392	62·14	62·60
Diamylic "	- 9·92	-27·19	1·079	1·4438	71·48	71·80
Dicaprylic "	- 6·92	-24·77	0·9761	1·4500	98·57	99·42
Dimethylic acetylmalate	-22·92	-46·76	1·1975	1·4318	44·17	44·52
" propionylmalate	-22·94	—	—	—	—	—
" butyroylmalate	-22·44	-52·07	1·1317	1·4342	53·41	53·73
" isobutyroylmalate	-22·36	-51·86	1·1255	1·4310	53·35	53·73
" isovaleroylmalate	-22·39	-55·07	1·1034	1·4350	58·18	58·34
" chloracetylmalate	-23·30	-55·56	1·3862	1·4530	49·35	49·48
" bromacetylmalate	-22·40	-63·38	1·5072	1·4680	52·20	52·41
Diethylic acetylmalate..	-22·52	-52·25	1·1168	1·4295	53·61	53·73
" propionylmalate	-22·20	-54·62	1·0958	1·4308	58·09	58·33
" butyroylmalate	-22·22	-57·78	1·0736	1·4315	62·75	62·94
" isobutyroylmalate	-21·99	-57·17	1·0688	1·4285	62·65	62·94
" isovaleroylmalate	-22·07	-60·46	1·0605	1·4338	67·26	67·55
" bromacetylmalate	-22·48	-69·92	1·3936	1·4610	61·24	61·61
" bromopropionylmalate	-22·48	-73·05	1·3325	1·4561	66·31	66·22
" bromobutyroylmalate	-24·76	-83·93	1·3059	1·4568	70·68	70·82
" bromisobutyroylmalate	-22·57	-76·50	1·2850	1·4520	71·17	70·82
" ethoxysuccinate	- 1·44	- 3·13	1·1045	1·4320	54·10	53·55
Dipropylic acetylmalate.	-22·85	-59·40	1·0724	1·4315	62·82	62·94
" chloracetylmalate	-23·52	-69·26	1·1566	1·4465	67·96	67·88
" butyroylmalate	-22·40	-64·50	1·0417	1·4348	72·11	72·15
" isovaleroylmalate	-21·68	-65·47	1·0263	1·4352	76·81	76·75
" bromacetylmalate	-22·24	-75·41	1·3150	1·4608	70·71	70·82
Diisobutyric acetylmalate	-21·88	-63·01	1·0362	1·4330	72·32	72·15
" butyroylmalate	-21·68	-68·52	1·0146	1·4352	81·30	81·35
" isovaleroylmalate	-19·91	-65·70	1·0045	1·4353	85·78	85·96
" bromacetylmalate	-20·38	-74·80	1·2022	1·4520	82·36	80·03

Substance.	$[\alpha]_D$.	$[M]_D$.	d .	n .	R.	
					Observ.	Calc.
Chlorosuccinic chloride..	+ 29 ·53	+ 55 ·93	1 ·5002	1 ·4840	36 ·12	35 ·73
Dimethylic chlorosuccinate	+ 41 ·42	+ 74 ·76	1 ·2555	1 ·4436	38 ·16	38 ·40
Diethylic chlorosuccinate	+ 27 ·50	+ 57 ·33	1 ·1493	1 ·4372	47 ·55	47 ·61
Dipropylic „	+ 25 ·63	+ 60 ·61	1 ·0925	1 ·4412	57 ·19	56 ·82
Diisobutyric chlorosuccinate	+ 21 ·57	+ 57 ·05	1 ·0524	1 ·4403	66 ·28	66 ·03
Diamylic chlorosuccinate	+ 21 ·56	+ 63 ·07	1 ·0319	1 ·4436	75 ·24	73 ·23
Dimethylic bromosuccinate	+ 51 ·18	+ 114 ·37	1 ·5050	1 ·4618	41 ·32	41 ·33
Diethylic bromosuccinate	+ 40 ·96	+ 103 ·63	1 ·3550	1 ·4550	50 ·66	50 ·54
Dipropylic bromosuccinate	+ 38 ·05	+ 106 ·9	1 ·3010	1 ·4592	59 ·07	59 ·74
Diisobutyric bromosuccinate	+ 23 ·56	+ 72 ·80	1 ·2394	1 ·4580	68 ·03	68 ·94

ently distributed in the two cases between the four molecular groups, have sometimes nearly the same, and sometimes very different rotatory powers; in some cases, a considerable alteration in the mass of a group causes only a very small change in the rotatory power.

In addition to the specific and molecular rotations of the various substances determined at 20°, the table gives the densities d , at 20° referred to water at 0°, and the refractive indices n , for the D line at 20°, together with the observed and calculated molecular rotations R , obtained from Gladstone's formula.

W. J. P.

Optically Active Derivatives of Phenylacetic acid : Optical Superposition. By PAUL WALDEN (*Zeit. physikal. Chem.*, 1895, 17, 705—724; compare preceding Abstr.).—Starting with mandelic acid, in which the four groups attached to the asymmetric carbon atom have the masses 77, 45, 17, and 1, the author has prepared and examined the rotatory powers of a number of derivatives in which the masses of the above four groups vary; from the data thus obtained, the author shows that, as in the case of the malic acid derivatives, the product of asymmetry affords no criterion of the rotatory power, and deduces conclusions similar to those stated in the preceding abstract. The carboxyl group in mandelic acid is of practically the same mass as the group CONH_2 in mandelamide, so that these two substances should have almost the same rotatory power. Table I, however, shows $[\alpha]_D$ to be very different in the two cases. Similarly, tartaric diamide has a specific rotation in water or saturated boric acid solution of $[\alpha]_D = +108^\circ$ to $109\cdot4^\circ$, whilst for tartaric acid $[\alpha]_D = +14\cdot93$.

The very different specific rotations possessed by ethylic mandelate in acetone and carbon bisulphide solutions seem not to be due to a difference in molecular weight, as this substance depresses the boiling point of the two solvents normally.

TABLE I.

Substance.	$[\alpha]_D$.	$[\alpha]_D$.	$[\alpha]_D$.
Mandelic acid	-153.1° in H ₂ O...	-148.0° in COMe ₂	
Mandelamide.....	- 66.7 „ COMe ₂	—	
Methylic mandelate ..	-110.2 „ COMe ₂	-214.1 in CS ₂ .	
Ethylic „ ..	-123.12 liquid ...	- 88.8 „ COMe ₂	-180.0° in CS ₂ .
Isobutyric „ ..	-100.73 „ ...	-145.0 „ CS ₂ .	
Amylic „ ..	- 96.46 „ ...	—	
Methylic acetylmande- late	-146.37 „ ...	—	
„ propionyl- mandelate	-135.5 „ ...	—	
Ethylic propionyl- mandelate	-113.7 „ ...	-110 in CHCl ₃ ..	-129 in CS ₂ .
„ valeroylman- delate	- 97.06 „ ...	-117 „ CS ₂ .	
Acetylmandelic acid..	-156.4 in COMe ₂ .	—	
Phenylchloroacetic acid	+131.8 „ C ₆ H ₆ ..	+131.3 in CS ₂ ...	+107.9 in CHCl ₃ .
„ chlor- ide	+158.3 „ CS ₂	—	
Methylic phenylchlor- acetate	+107.55 liquid ...	—	
Ethylic phenylchlor- acetate	+ 25.19 „ ...	+ 26.39 in CS ₂ ..	
Propylic phenylchlor- acetate	+ 23.94 „ ...	—	
Amylic phenylchlor- acetate	+ 23.31 „ ...	—	
Phenylbromoacetic acid	+ 45.4 in C ₆ H ₆ ..	—	
Methylic phenylbrom- acetate	+ 29.82 liquid ...	—	
Ethylic phenylbrom- acetate	+ 16.56 „ ...	—	
Isobutyric phenyl- bromacetate	+ 9.77 „ ...	—	
Phenylbromoacetic bro- mide	+ 44.53 „ ...	—	

In order to test the principle of "optical superposition," which states that the several optically active groups in a given molecule act additively and in such a way that the specific rotation of a substance becomes the algebraic sum of the specific rotations of two of its stereoisomerides, the author has examined a number of suitable salts and obtained results which are summarised in Table II. The density d , the molecular rotation $[M]_D$, and the specific rotation $[\alpha]_D$, of each series of three salts was determined; the last column contains the specific rotation of the third salt of each series calculated as the sum of the specific rotations of the first and second. The specific rotations of lævo-amyllic lævo-lactate is thus the sum of the specific rotations of inactive amyllic lævo-lactate and lævo-amyllic inactive lactate; the agreement, as will be seen, is very close.

TABLE II.

	<i>d.</i>	[<i>M</i>] _{D.}	[α] _{D.}	
			Observ.	Calc.
<i>i</i> -amylic <i>l</i> -lactate	0·9719	— 10·21°	— 6·38°	—
<i>l</i> - „ <i>i</i> - „	0·9672	+ 4·22	+ 2·64	—
<i>l</i> - „ <i>l</i> - „	0·9667	— 6·29	— 3·93	— 3·74
<i>i</i> -amylic <i>l</i> -mandelate	1·0531	— 214·14	— 26·46	—
<i>l</i> - „ <i>i</i> - „	1·0520	+ 6·12	+ 2·76	—
<i>l</i> - „ <i>l</i> - „	1·0530	— 208·72	— 94·02	— 93·70
<i>i</i> -amylic <i>d</i> -phenylchloracetate	1·0828	+ 56·08	+ 23·31	—
<i>l</i> - „ <i>i</i> - „	1·0832	+ 7·78	+ 3·23	—
<i>l</i> - „ <i>d</i> - „	1·0826	+ 64·42	+ 26·79	+ 26·54
<i>i</i> -diamylic <i>l</i> -malate	1·0790	— 27·19	— 9·92	—
<i>l</i> - „ <i>i</i> - „	1·0180	—	+ 3·50	—
<i>l</i> - „ <i>l</i> - „	1·0176	— 18·85	— 6·88	— 6·42
<i>i</i> -diamylic <i>d</i> -chlorosuccinate	1·0319	+ 67·03	+ 21·56	—
<i>l</i> - „ <i>i</i> - „	1·0314	+ 10·98	+ 3·75	—
<i>l</i> - „ <i>d</i> - „	1·0303	+ 73·53	+ 25·15	+ 25·31
<i>i</i> -diamylic <i>d</i> -tartrate	1·0637	—	+ 14·10	—
<i>l</i> - „ racemate	1·0640	—	+ 3·37	—
<i>l</i> - „ <i>d</i> -tartrate	1·0636	—	+ 17·73	+ 17·47

W. J. P.

Optically Active Halogen Compounds. By PAUL WALDEN (*Ber.*, 1895, 28, 2766—2773).—See this vol., i, 139.

The Birotation of Glucose. By HEINRICH TREY (*Zeit. physikal. Chem.*, 1895, 18, 193—218).—The birotation phenomena of glucose were investigated in aqueous and other solutions, both the anhydride and the hydrate being employed. In solutions in methylic and ethylic alcohol, birotation occurs as in water, but more slowly, whilst also the final value is higher than in aqueous solution, both initial and final values being higher in ethylic than in methylic alcohol. By the addition of water to the alcoholic solution, the retrogression was accelerated and the final value also reduced to an extent corresponding with the quantity of water added. Chemically indifferent compounds cause a retardation in the methylic alcohol solution of the anhydride, and a slight increase of the end value. In aqueous solutions of both anhydride and hydrate, acids cause an acceleration, the effects in this respect being in the same order as the affinity constants. By the addition of hydrogen chloride, even in small quantities, to the methylic alcohol solution, the rotation was reduced to zero, this being probably due to decomposition. By the solution in water of the amorphous residue left on evaporating an alcoholic solution, the end value of the rotation was at once obtained, and the author considers that his experiments indicate that the explanation of the birotation is to be sought for, not in the hydration of the compound,

but in a change from a crystalline to an amorphous variety, or in some such alteration of the molecular configuration. (Compare also Levy, *Abstr.*, 1895, ii, 586.)

L. M. J.

Theory of the Decomposition of Racemic Compounds. By CHR. WINTHER (*Ber.*, 1895, **28**, 3000—3023).—The author enunciates a general theory respecting the decomposition of racemic compounds into their optically active constituents either by means of active bases or by crystallisation. The theory only holds good for compounds in the solid state or in saturated or supersaturated solutions. The atoms or groups attached to the asymmetric carbon atom of one molecule are supposed to have certain affinities for the corresponding atoms or groups in a second molecule. These affinities the author terms "secondary," and supposes they are of two kinds. For example, in the case of a compound containing an asymmetric carbon atom to which hydrogen and hydroxyl are attached, the affinity between the H and H, or between OH and OH, is termed "racemic" affinity, and that between H and OH "contrary" affinity. If, under given circumstances, the racemic affinities of a compound are greater than the contrary affinities, it will be found impossible to split up the compound into its active constituents by the above means; in order to bring about such a decomposition, energy, either thermal or chemical, must be supplied to the system. Under a certain set of conditions there will always be an equilibrium between the two secondary affinities. It is shown that the theory agrees with the facts hitherto known regarding the decomposition of racemic compounds, and the paper concludes with an index to the literature of the subject.

J. J. S.

Flames and Illuminating Gases. By C. BOHN (*Zeit. physikal. Chem.*, 1895, **18**, 219—239).—The form of Bunsen burner devised by Teclu (*Abstr.*, 1892, 768) was used for the experiments. The appearance of the flame is first described, five parts being recognised—(1) the inner cone surrounded by (2) the mantle, around which lie (3) the outer cone with (4) its border, above which is (5) the cap. The variations in the several parts according to the air supply is recorded, and then the spectroscopic examination. The cap gave a feeble continuous spectrum with no red and but little blue; the border also gave a continuous spectrum with the red feebly developed; that of the outer cone was also continuous, dark and bright lines being absent, and the red being well developed. The mantle, however, gave a band spectrum with well-marked green and indigo or violet bands, and under some circumstances a blue stripe also, and a dark band close to the D lines. The inner cone appeared to give a feeble band spectrum, most probably, however, due to the mantle. The author considers the mantle to be the place of explosive combustion and of the greatest development of energy, although not necessarily the hottest part of the flame. Sulphur, hydrogen, carbon bisulphide (by a wick), and carbonic oxide were also burnt, and for all these flames, the spectra were continuous. The measurements of the band spectra are recorded, the results being compared with those obtained by Swan. The spectroscopic measurements are also

recorded in the case of Geissler tubes containing various carbon compounds, and the author concludes that the discontinuous spectra of carboniferous gases are not identical, the differences being greater than those occasioned by alterations of temperature and density. It is hence not possible to define a carbon band spectrum, and even sharpness of the less refrangible edge of the bands, and gradual fading of the more refrangible edge, does not exist with all carbon compounds.

L. M. J.

Cause of Luminosity in the Flames of Hydrocarbon Gases.

By VIVIAN B. LEWES (*Proc. Roy. Soc.*, 1895, **57**, 450—468).—According to the "solid particle" theory of luminosity, it is to be expected that the luminosity of different flames of the same size and burning from the same kind of jet, would be governed (1) by the temperature of the flame; (2) by the number of carbon particles in a given area.

In order to determine the temperatures of different flames, the author has made use of a very small and thin Le-Chatelier thermocouple. Preliminary experiments showed that the diameter of the wire seriously affected the temperature recorded, and the author concludes that the temperatures indicated by the finest wires which can be used without fusing are probably 100—200° too low. The following results were obtained.

	Acetylene.	Ethylene.	Coal gas.
Non-luminous zone	459°	952°	1023°
Commencement of luminosity	1411	1340	1658
Near top of luminous zone	1517	1865	2116

As regards luminosity, however, the three gases stand in exactly the reverse order; and as there appears to be no apparent relation between the temperature of the flame, or the probable number of carbon particles contained in it, and its illuminating value, it is suggested that the luminosity must be in great part governed by some thermochemical changes taking place in the flame and yet not appreciably affecting the average temperature. It is thought that as acetylene is formed when hydrocarbons are burnt, and as it is an endothermic substance, the heat liberated during its decomposition endows the carbon particles with a high incandescence. In support of this view, the author shows that acetylene, when decomposed by a detonator or merely by strongly heating it in a glass tube, develops light. It is also shown that acetylene, when largely diluted with hydrogen, carbonic oxide, carbonic anhydride or nitrogen, burns with a non-luminous flame (compare P. Frankland, *Trans.*, 1884, 30 and 227). It has been found possible to make such mixtures burn with luminous flames by externally increasing the temperature.

The luminosity of a flame, therefore, depends not so much on the percentage of acetylene in the gas, but rather as to whether there are many points at which the temperature is sufficiently high to bring about decomposition of the acetylene. The flame of alcohol contains as much acetylene as a good coal gas flame, and yet is non-, or only

slightly, luminous, because the temperature is too low to decompose the acetylene. When burnt in oxygen, the flame becomes brightly luminous, owing to the increase in temperature. Cyanogen, which is even more endothermic than acetylene, burns with a non-luminous flame. This is due to the fact that cyanogen requires a much higher temperature before it is decomposed, and it is shown that when sufficiently strongly heated, it can be made to burn with a luminous flame.

J. J. S.

Red and Yellow Mercuric Oxides. By WILHELM OSTWALD and THOR MARK (*Zeit. physikal. Chem.*, 1895, **18**, 159—160).—The experiments of Varet proved the identity of the heats of formation of the two mercuric oxides, hence the total energies are equal for these compounds (Abstr., 1895, ii, 305). A galvanic cell of mercury—red oxide—caustic potash—yellow oxide—mercury, was found by the author to give no E.M.F., whilst, also, no change of the E.M.F. of various cells occurred when red and yellow oxides replaced one another. Hence, the author points out, the free energy of the two forms are also equal, and the compounds are not isomeric but identical.

L. M. J.

Peroxide Electrodes. By OLIN FREEMAN TOWER (*Zeit. physikal. Chem.*, 1895, **18**, 17—50).—Examination of various peroxide electrodes showed those of lead, silver, and thallium to be unavailable, as with the first a long time is necessary before a constant E.M.F. is obtained, whilst the two peroxides last mentioned are unstable and readily acted on by dilute acid solutions. Manganese peroxide, being free from the above disadvantages, was therefore selected for the experiments. The E.M.F. with this electrode is given by the formula

$$n\epsilon_0\pi = Rt \log (C_m C_0^4 / C_m' C_0'^4),$$

where $C_m + C_0$ are the concentrations of the manganese and hydroxyl ions respectively, the other letters having the usual significance. In acid solutions, $C_0 \times C_H$ being constant. k/C_H may be substituted for C_0 , and the formula reduces to

$$\pi = -0.0286 \log (C_m C_H^4 / C_m' C_H'^4).$$

Experiments were made with solutions of varying nitric acid and manganous nitrate content; the observed and calculated results show satisfactory agreement, the differences being probably due to incomplete dissociation. As theoretically indicated, the effect of the salt concentration was found to be four times that of the acid. Experiments were also made with phosphoric, malonic, tartaric, formic, acetic, salicylic, orthamidobenzoic, mono-, di-, and tri-chloroacetic acids, the concordance between the observed and calculated numbers being again, for the most part, satisfactory. The influence of temperature was next determined. This, in the case of nitric and sulphuric acids, is very slight, rather more for phosphoric and the chloroacetic acids, and very marked with acetic, formic, and tartaric acids. No reason for these differences is, however, indicated. The determination of the E.M.F. is also employed for the determination of the degree of dissociation of the sodium salts of 16 organic acids at varying concentrations, and the results compared with those obtained by Trevor (Abstr., 1893,

ii, 62). The only cases in which satisfactory agreement is not obtained are those of the phthalates and isophthalates, where the author finds the former salt to be the more highly dissociated. Barium salts were also employed in a few cases, and the dissociation is determined for acid sulphates of potassium, magnesium, sodium, aluminium, and copper, hydrogen sodium selenate, and dihydrogen sodium phosphate. In alkaline solutions, the electrolyte is a solution of $\text{Mn}(\text{OH})_2$, hence $C_m \times C_0^2 = k$, and $C_m C_0^4 = k/C_0^2$, hence $\pi = -0.0286 \log (C_0^2/C_0^2)$. The availability of the formula is shown by experiments with potassium, sodium, barium, strontium, calcium, and ammonium hydroxides. By the use of a perfectly neutral solution, the dissociation of pure water is obtained as 4.4×10^{-8} , a number which, although of the same degree of magnitude, is smaller than that which has been obtained by other methods.

L. M. J.

Potential Differences between Metals and Electrolytes. By GEORG MEYER (*Ann. Phys. Chem.*, 1895, [2], 56, 680—699).—Rothmund (Abstr., 1825, ii, 35) has calculated the E.M.F. of various cells from his electro-capillary measurements of the potential differences between the metals and electrolytes composing them, and in a number of cases the values thus obtained do not agree with those directly measured. The author has repeated, and, in general, confirmed Rothmund's measurements. He therefore concludes that the E.M.F. of a cell $M_1 | F_1 | F_2 | M_2$, composed of the metals M_1 and M_2 and the electrolytes F_1 and F_2 , is not given by the difference between the forces necessary to produce the maximum surface tension of polarisation of M_1 in F_1 and of M_2 in F_2 . The potential difference between the two metals and two electrolytes must be taken into account, and to the difference of E.M.F. above spoken of must be added the potential difference between two dropping electrodes, which, containing M_1 and M_2 , are respectively placed in the electrolytes F_1 and F_2 . It is only when this last term approaches zero in value that it can be neglected.

H. C.

Electro-capillary Properties of Dilute Sulphuric acid. By A. GOUY (*Compt. rend.*, 1895, 121, 765—768).—The author has made a number of determinations of the relationship between the height h of the column of mercury balanced by electro-capillary forces, and the difference of potential V between the mercury and the electrolyte, using solutions of sulphuric acid of various concentrations as the electrolyte. The values of h decrease with the concentration of the solution, but, in the more concentrated solutions, exact measurements become impossible, owing to the occurrence of electrolysis. The second derived function d^2h/dV^2 is always negative, so that the curve of h has no point of inflexion, and does not tend to any limiting value. The actual value of the function is not constant, but is subject to complex variation.

H. C.

The Passage of Electricity through Gases. By OTHO LEHMANN (*Zeit. physikal. Chem.*, 1895, 18, 97—117).—Experiments are described on the electric discharge through various gases, vacuum tubes,

mixed gases with different forms of electrodes, and the discharge in a strong magnetic field. The paper is illustrated by a number of figures of discharge phenomena, and the author considers the views of Goldstein and Hertz, that the discharge takes place into the ether and not into the gas, to be erroneous.

L. M. J.

Relation between the Dielectrical Constants of Gases and their Chemical Valency. By ROBERT LANG (*Ann. Phys. Chem.*, 1895, [2], 56, 534—545).—Between the dielectrical constant, K , of a gas, that of the ether being unity, and the sum of the valencies of the atoms in the molecule of the gas, s , the author finds that there is the following general relationship.

$$\frac{K-1}{s} 10^6 = 123.$$

This relationship does not always hold if the simple chemical molecule of the gas is taken, but, in such cases, the assumption is made that a number of these molecules are combined to form a complex group, when agreement is obtained. The values of K are taken for 0° and 760 mm. pressure. The term *dielectrical valency constant* is proposed for the constant, the value given above for this being provisional only.

H. C.

Determination of High Resistances. By MARGARET E. MALTBY (*Zeit. physikal. Chem.*, 1895, 18, 133—158).—A method for the determination of high electrolytic resistances is described, previous methods being considered unsatisfactory. A Wheatstone bridge is employed with four carefully calibrated adjustable electrolytic resistances, and when a balance is obtained, the unknown resistance is placed in one arm (1) in series (2) parallel, and that resistance again adjusted for a balance. Full details of the construction, calibration, and working of the instruments are given in the paper. Comparison of numbers obtained with those due to Kohlrausch indicates the availability of the method. Experiments are recorded with a solution of hydrogen chloride in ether at its critical temperature, the resistance increasing from 641 divisions at 20° to 24,180 at 197°, at which temperature critical phenomena were observed. Solutions of trichloroacetic acid in ether, and of potassium chloride in water, were also examined at high temperatures. The former gave a continuous decrease until 75°, when the resistance commenced to increase; with the latter salt, the resistance decreased regularly to 297°. The method is stated to be available for the determination of the conductivity of pure water, but no measurements are recorded.

L. M. J.

Determination of some Conductivities. By A. E. BAUR (*Zeit. physikal. Chem.*, 1895, 18, 183—184).—The conductivity of tetrazole compounds was first examined with the following results: Tetrazole, CN_4H_2 , $\mu_{1024} = 37.96$; amidotetrazotic acid, $\text{C}_2\text{H}_6\text{N}_{10}$, $\mu_{1024} = 11.61$; sodium azotetrazole, $\text{C}_2\text{N}_{10}\text{Na}_2.5\text{H}_2\text{O}$, $\mu_{1024} = 103.6$; sodium amidotetrazotate, $\text{CH}_2\text{N}_5\text{Na}.3\text{H}_2\text{O}$, $\mu_{1024} = 93.27$. The conductivities of the chlorates of caesium, rubidium, and potassium were found to be 137.5, 134.9, and 129.9 respectively (μ_{1024}), and hence, taking the ion velocity of

potassium as 70.6 and $\mu_{\infty} = \mu_{1024} + 3$, the following ion velocities are obtained: Rb, 75.6; Cs, 78.2; ClO_4 , 62.3. The values of the velocities of the metallic ions were also determined by means of the chlorides with the results Rb, 76.5; Cs, 79.3. L. M. J.

The Dilution Law of Salts. By JACOBUS H. VAN'T HOFF (*Zeit. physikal. Chem.*, 1895, **18**, 300—304).—Rudolphi found (Abstr., 1895, ii, 490) that the relation between the molecular conductivity and the concentration is given by the expression $k = \frac{(\lambda_r/\lambda_{\infty})^2}{\sqrt{v(1 - \lambda_r/\lambda_{\infty})}}$ instead of by Ostwald's expression $k = \frac{\lambda_r/\lambda_{\infty}}{v(1 - \lambda_r/\lambda_{\infty})}$. The author shows that in Rudolphi's experiments a slightly better constancy of k is obtained by the expression $\frac{(\lambda_r/\lambda_{\infty})^3}{\sqrt{v(1 - \lambda_r/\lambda_{\infty})}}$, which leads immediately to the equation $c_i^3/c_s^2 = \text{constant}$ where c_i and c_s are the concentrations of ions and non-dissociated substance respectively, although, as the author points out, the physical interpretation is not very clear. L. M. J.

Specific Heat of Mercury between 0° and 30°. By ADOLFO BARTOLI and ENRICO STRACCIATI (*Gazzetta*, 1895, **25**, i, 380—388).—After a summary of the work previously done, the authors give an account of their determination of the specific heat of mercury between 0° and 30° made by cooling a mass of platinum, previously heated in a steam bath, in water, and in pure mercury, successively; using the values for the specific heat of water previously obtained by them (Abstr., 1895, ii, 5), the specific heat of mercury between 0° and 30° is given by the equation

$$C = 0.033583 + 0.00000117 T - 0.0000003T^2,$$

in which T is the temperature for which the specific heat C is required. The numbers agree well with those obtained by Naccari and by Winkelmann. W. J. P.

Specific Heats of Platinum, Silver, Tin, Lead and Copper. By ADOLFO BARTOLI and ENRICO STRACCIATI (*Gazzetta*, 1895, **25**, i, 389—393; compare preceding abstract).—The authors have obtained the following values for the specific heats of various metals between 15° and 100° as the means of a large number of measurements; the values are referred to water at 15°, and the impurities are given in percentages.

Platinum (containing traces of Ir)	0.032238
Silver (" 0.047 Cu and 0.016 Au) ..	0.056250
Tin (" 0.030 Fe and 0.008 Pb) ..	0.055550
Lead (" 0.030 Tl and traces of other metals)	0.030887
Copper (" 0.12 Sn and 0.12 Au)	0.093392
" (" 0.005 Sn and traces of other metals)	0.093045

W. J. P.

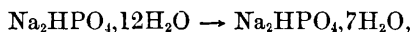
Latent Heats of Vaporisation of Ketones and other Carbon Compounds. By WLADIMIR F. LOUGUININE (*Compt. rend.*, 1895, **121**, 556—558).—In the following table, column I contains the boiling point under a pressure of 760 mm., column II the latent heat of vaporisation, and column III the value of the constant in Trouton's expression $MS/T = \text{constant}$, where M is the molecular weight, S the latent heat of vaporisation, and T the boiling point on the scale of absolute temperatures.

	I.	II.	III.
Dipropyl ketone	143·90°	75·94 Cal.	20·76
Methyl butyl ketone.....	127·61	82·91 „	20·70
Diethyl ketone	102·46	90·54 „	20·74
Methyl isopropyl ketone....	94·04	88·67 „	20·78
Methyl ethyl ketone.....	79·54	103·44 „	21·13
Decane.....	159·45	60·83 „	19·98
Octane (normal).....	124·90	70·92 „	20·32
Diethylic carbonate.....	126·28	72·80 „	21·53
Dimethylic carbonate.....	90·30	87·87 „	21·76

These results, with those of previous observers, show that in each group of compounds the value of MS/T is almost constant, whilst it differs considerably in different groups. Ostwald has already pointed out that this expression makes it possible to calculate the latent heat of vaporisation with a probable error of not more than 15 per cent. Since, however, the variations in its value are very small in a group of homologous and isomeric compounds, the latent heats of vaporisation of all the members of a series can be calculated with an error of not more than 1 to 1·5 per cent., when the value has been experimentally determined for one member of the series.

C. H. B.

Determination of Transition Points. By A. E. BAUR (*Zeit. physikal. Chem.*, 1895, **18**, 180—182).—The transition temperature was determined by the electrical method of Cohen and Bredig (*Abstr.*, 1894, ii, 407) in the change



and the method was used to investigate the cause of the colour change experienced by the solution of the double salt $\text{HgI}_2 \cdot 2\text{AgI}$ at about 50°. The transition temperature in the first case was found to lie between 36·5 and 36·8, whilst in the second case the colour change from yellow to red is due to the formation of mercuric iodide owing to the decomposition of the double salt.

L. M. J.

Improved Calorimeter for the Application of the Method of Mixtures. By F. A. WATERMAN (*Phil. Mag.*, 1895, [5], **40**, 413—421).—For the purpose of avoiding the radiation correction in the determination of the specific heat of solids by the method of mixtures, Hesehus has suggested that the calorimeter cup be introduced into the bulb of an air thermometer and maintained at a constant temperature by the introduction of a sufficient amount of cold water, of

known temperature, immediately after the introduction of the heated solid. By this means, both the radiation correction and the water equivalent of the calorimeter cup are avoided, the heat received by the cold water being equal to that given out by the heated substance.

The author has constructed a calorimeter on the above principle. The water cooler and dropper is supported upon a vertical rod in such a manner that it may be quickly turned about the rod as an axis, and may deliver water directly to the calorimeter cup. An electric heater is supported upon a second vertical rod and may be turned about the rod as an axis until it is directly over the calorimeter cup, allowing the heated body to be transferred directly to the cup. A summary of some trial determinations made with this apparatus is given, showing that it gives concordant results. H. C.

Thermal Unit. By ERNEST H. GRIFFITHS (*Phil. Mag.*, 1895, [5], 40, 431—454).—The capacity for heat, of water, has been invariably adopted in defining the thermal unit, and its capacity at 0° , 4° , 15° , and its mean capacity from 0° to 100° , have been variously selected as standards by different observers. This selection is unfortunate, as at present our knowledge of the comparative value of these standards is vague, and comparison of the results of the different investigators becomes impossible. The range 10° to 30° is of particular importance, as the majority of thermal determinations are expressed in terms of the capacity of water at some point within this range, and as a consequence great attention has been devoted to it; but in spite of this, a comparison of the results of those observers whose work appears to be most worthy of attention, shows that a discrepancy which may be as great as 1 in 300 exists between their results. Even greater uncertainty attaches to the determination of the "mean calorie," as the determinations of the ratio of the mean calorie to the thermal unit at 15° , give results varying from 1.013 to 0.9957, a difference of 1 part in 60. It appears, therefore, that the endeavours to establish the heat capacity of water as the standard of calorimetric measurements have, so far, not met with success.

It has been pointed out by Gray, that even if the specific heat of water was accurately known it would not, for any reason, be arithmetically commensurable with any other definite physical quantity, but it would be a purely arbitrary quantity. But it is evident that the ideal thermal unit should be a natural, not an arbitrary, one, and have some real relation with other units of energy. Further, it should not be dependent on the observations or conclusions of any one investigator; it should be of a convenient magnitude, and should cause as little disturbance as possible in the numerical values resulting from our present system of thermal measurements. The author proposes that the value of this ideal unit should be first defined, that value being some convenient multiple of an absolute unit. A first approximation could then be made to the physical unit thus selected, and this improved, if necessary, by subsequent measurements. It is proposed that the unit adopted should be a thermo-dynamic one, and that this ideal unit should be termed a "Rowland." The name

"Therm" is taken to indicate the quantity of heat required to raise 1 gram of water (measured in vacuum) through 1° of the nitrogen thermometer at a temperature t° of that thermometer. The Rowland should be of such a magnitude that a therm at some convenient temperature would be its heat equivalent. The particular therm which is the exact equivalent of a Rowland could be denoted by the phrase "standard therm."

(This paper was read at the 1895 meeting of the British Association. The consideration of the whole matter has been referred to the Committee on Electrical Standards.) H. C.

Heats of Combination of Substances in the Liquid and Solid Conditions. By P. SPENCER U. PICKERING (*Phil. Mag.*, [5], 39, 510).—The author has investigated several so-called molecular compounds to ascertain whether, as in the case of the monohydrate of sulphuric acid, their heats of formation were the same in both solid and liquid conditions. Their heats of combination as liquids were determined directly, and the value for the solids deduced indirectly from the heats of fusion of the constituents and compounds. The heat capacities of the substances in both conditions had also to be determined in order to reduce the heats of fusion to the same temperature. The heat of combination thus calculated is, however, the true heat of combination only if the heat of fusion of the compound is equal to the sum of those of its constituents, and the results obtained by the author prove that this is not the case, the heat of fusion of the compound being generally the smaller quantity. The true heat of combination in the solid condition can, therefore, not be obtained.

The substances investigated were: Compounds of sulphuric acid, pinacone, stannic bromide, and sodium hydroxide with water; benzene with azobenzene; and dinitro- and meta-dinitrobenzene with naphthalene. The existence of the two last-mentioned compounds was investigated and established by series of freezing point determinations; so also was the existence of the octohydrate of stannic bromide, which had not before been isolated. S. U. P.

Combination of Mercuric Cyanide with Iodides. By RAOUL VARET (*Compt. rend.*, 1895, 121, 499—501).—The first column gives the heat of dissolution of the salt in water; the second, the heat developed on mixing solutions of mercuric cyanide and the particular iodide; and the third the heat of formation of the solid salt from its proximate constituents (solid salts and liquid water).

	1.	2.	3.
$\text{Hg}(\text{CN})_2, 2\text{NaCN}, \text{HgI}_2, 4\text{H}_2\text{O} \dots$	-22.8	+5.3	+24.7 Cal.
$\text{Hg}(\text{CN})_2, 2\text{NH}_4\text{I}, \text{HgI}_2, \frac{1}{2}\text{H}_2\text{O} \dots$	-23.5	+4.5	+15.0 "
$\text{Hg}(\text{CN})_2, 2\text{LiCN}, \text{HgI}_2, 7\text{H}_2\text{O} \dots$	-20.7	+5.5	+50.0 "
$\text{Hg}(\text{CN})_2, \text{Ba}(\text{CN})_2, \text{HgI}_2, 6\text{H}_2\text{O} \dots$	-22.0	+5.3	+31.6 "
$\text{Hg}(\text{CN})_2, \text{Sr}(\text{CN})_2, \text{HgI}_2, 7\text{H}_2\text{O} \dots$	-21.8	+5.5	+41.8 "
$\text{Hg}(\text{CN})_2, \text{Ca}(\text{CN})_2, \text{HgI}_2, 7\text{H}_2\text{O} \dots$	-22.4	+5.5	+49.5 "
$\text{Hg}(\text{CN})_2, \text{Mg}(\text{CN})_2, \text{HgI}_2, 8\text{H}_2\text{O} \dots$	-20.0	+5.3	+69.1 "
$\text{Hg}(\text{CN})_2, \text{Cd}(\text{CN})_2, \text{HgI}_2, 8\text{H}_2\text{O} \dots$	-22.5	+2.0	+17.3 "

At 30° , the solutions of the iodocyanides, unlike those of the chloro-

cyanides and bromocyanides (this vol., i, 3; ii, 88), are strongly alkaline to litmus, and give the isopurpurate reaction with picric acid, and hence it follows that they contain salts of the type $\text{Hg}(\text{CN})_2$, $\text{M}''(\text{CN})_2 \cdot \text{HgI}_2$. The conversion of the system $2\text{Hg}(\text{CN})_2 + \text{M}''\text{I}_2$, into $\text{Hg}(\text{CN})_2 + \text{M}''(\text{CN})_2 + \text{HgI}_2$, absorbs about -9.3 Cal. in solution, whilst the heat of formation of the double cyanides, $\text{Hg}(\text{CN})_2 \cdot \text{M}''(\text{CN})_2$, is $+12.4$ Cal., and their union with yellow mercuric iodide develops $+2.3$ Cal.

C. H. B.

Lithium, Magnesium, and Copper Cyanides. By RAOUL VARET (*Compt. rend.*, 1895, **121**, 598—599).—*Lithium Cyanide*.—The heat of neutralisation of hydrocyanic acid solution by lithia is $+5.85$ Cal., and hence

$\text{Li sol.} + \text{CN gas} + \text{Aq} = \text{LiCN diss.}$ develops $+65.12$ Cal.

Magnesium Cyanide.—The heat of neutralisation $[\text{Mg}(\text{OH})_2]$ is $+3.0$ Cal., and hence

$\text{Mg sol.} + 2\text{CN gas} + \text{aq.} = \text{Mg}(\text{CN})_2$
diss. develops $+112.0$ Cal.

Cuprous Cyanide.

$\text{Hg}(\text{CN})_2$ diss. + Cu_2I_2 sol. = HgI_2 (red)
+ $\text{Cu}_2(\text{CN})_2$ develops $+12.8$ Cal.
 $\text{Cu}_2\text{O sol.} + 2\text{HCN diss.} = \text{Cu}_2(\text{CN})_2$ sol.
+ $\text{H}_2\text{O liq.}$ „ $+28.8$ „
 Cu_2 sol. + $2\text{CN gas} = \text{Cu}_2(\text{CN})_2$ sol. „ $+29.8$ „

Hydrogen cyanide displaces hydrogen chloride from cuprous salts with development of $+13.6$ Cal., and hydrogen bromide with development of $+10.8$ Cal., but is displaced by hydrogen iodide with development of $+3.2$ Cal. These phenomena are analogous to those observed by Berthelot with mercuric oxide, and by the author with mercurous oxide; but whereas mercuric and mercurous oxides behave similarly, cupric oxide differs from cuprous oxide in that the heats of neutralisation of the former by hydrogen chloride, bromide, and iodide are practically identical.

C. H. B.

Depression of the Melting Point of Sodium Sulphate by the addition of Foreign Substances. By RICHARD LÖWENHERZ (*Zeit. physikal. Chem.*, 1895, **18**, 70—90).—The effect of non-electrolytes in lowering the melting point of sodium sulphate was first determined, urea, glycocine, cane sugar, formamide, and glycerol being employed, and the mean value for the depression constant so obtained was 32.6 . The effect of sodium salts was next investigated, and, as might be expected, they behaved practically as non-electrolytes, sodium phosphate giving the highest value (37.8), whilst the results indicate that the formula of sodium persulphate is $\text{Na}_2\text{S}_2\text{O}_8$. By the addition of sulphates (those of potassium, ammonium, and lithium), a double depression constant results. This may be due either to dissociation into K and KSO_4 ions, since neither of these is present in the solvent, or to an interaction; $\text{K}_2\text{SO}_4 + \text{Na}_2\text{SO}_4 = 2\text{KNaSO}_4$. Potassium chloride

and nitrate gave double values, which may be explained either by dissociation or interaction with the sodium sulphate, whilst potassium chromate and potassium carbonate gave depression constants equal to three times the normal, and capable of a similar explanation. By the determination of the solubility of sodium sulphate in (1) water, and in (2) a solution of urea, the temperature of transition to the anhydride was found to be (1) 32.46, (2) 29.26, the numbers obtained by the direct determinations being 32.39 and 29.26. The depression constant is calculated by use of the formula $k = 0.02TW$, and by Raoult's tension law, the values 36 and 33.8 being so obtained.

L. M. J.

Pressures of Saturation of Oxygen. By THADDEUS ESTREICHER (*Phil. Mag.*, 1895, [5], **40**, 454—463).—The author has measured the temperatures of the saturated vapour of oxygen under pressures lower than one atmosphere by means of a hydrogen thermometer. Three series of determinations were made, and the results, which are generally in close agreement with one another, are given in separate tables in the paper. The value of f in the Van der Waal's formula was calculated and compared with that given by a number of other associating and non-associating liquids at low pressures (compare Guye, *Abstr.*, 1895, ii, 153). The mean value for oxygen is about 2.45.

The author finds that the value of f always decreases with increase of temperature, both for associating and non-associating substances. The association of the molecules of the liquid has an influence on f , but is not the only reason of its increasing. Of 10 ethereal salts, six have values of f much higher than 3.06, although, according to Ramsay and Shields, they are not associated. Perhaps there is some relationship with the molecular weight, as the highest of the alcohols examined, isobutylic alcohol, has the highest f .

H. C.

Thermal Properties of Vapours: Alcohol Vapour and its Relationship to the Laws of Boyle and Gay-Lussac. By ANGELO BATELLI (*Ann. Chim. Phys.*, 1895 [7], **5**, 256—275).—The pressure of saturated ethylic alcohol vapour shows at high temperature a behaviour similar to that which the author has observed in several other substances, the pressure increasing as condensation proceeds and the liquid accumulates. The maximum pressures between the temperatures -16° and 240° may be represented by the formula of Biot,

$$\log p = a + b\alpha' + c\beta',$$

the values of the constants being

$$a = 5.0751023$$

$$b = 0.0435271 \quad \log b = \bar{2}.6387597 \quad \log \alpha = 0.00336681$$

$$c = -4.0217800 \quad \log c = 0.6044184 \quad \log \beta = \bar{1}.99683015$$

The critical constants obtained from the isothermal curves are: $t_c = 241.4^{\circ}$, $p_c = 47,348$ mm., and $v_c = 4.38$ c.c. The coefficients of dilatation of alcohol vapour under constant pressure increase as the temperature diminishes, this taking place the more rapidly the nearer the vapour is to the point of liquefaction. The absolute

values of the coefficients and their variations between the same limits of temperature increase with the increasing pressure of the vapour. From the isochoric curves, the values of dp/pdt , the coefficient of pressure change at constant volume, were calculated. The coefficient decreases with rising temperature, the variations becoming more marked the smaller the volume. As the volumes increase, the absolute value of the coefficient diminishes. The formula of Clausius in the modified form,

$$p = \frac{RT}{v - a} - \frac{mT^{-\mu} - nT^{\nu}}{(v + \beta)},$$

applies very closely to the results obtained with alcohol. H. C.

Vapour Pressure of Concentrated Solutions of several Salts, especially Lithium and Calcium Nitrates. By JOHN WADDELL (*Chem. News*, 1895, **72**, 201—203).—Into a wide-mouthed, closely stoppered bottle of about 200 to 300 c.c. capacity three small test-tubes were introduced, one of which contained water or alcohol, and each of the others one of the salts to be experimented with. After some experience had been gained, the liquid was frequently added directly to the salts, and the third test-tube dispensed with. The salts were taken in molecular proportions, weighed in milligrams, but 1, 2, or 4 mols. of one salt were taken to 1 mol. of the other, the numbers obtained being all so reduced as to show the quantity of liquid taken up per molecule of each salt.

Experiments were first made with calcium and lithium nitrates. If a curve is plotted whose ordinates are the quantities of water absorbed respectively by the lithium and the calcium nitrate, it does not differ very much from a straight line, although it is slightly concave towards the axis of the lithium nitrate. The ratio of the water absorbed by the lithium nitrate to that absorbed by the calcium nitrate ranged from about four-fifths to five-sixths. As, if all the molecules of each salt were dissociated into their ions, there would be the same vapour pressure when the amount of water absorbed per molecule by the lithium and calcium nitrates is in the ratio 2 : 3, it may be assumed that the lithium nitrate is dissociated to a greater extent than the calcium nitrate. When alcohol was employed as the liquid to be absorbed, there was less uniformity than in the case of water. Each molecule of lithium nitrate absorbs approximately four-fifths as much alcohol as each molecule of calcium nitrate. This condition would be fulfilled if all the lithium nitrate were dissociated, and one quarter only of the calcium nitrate molecules. A series of experiments was instituted for the purpose of comparing the nitrates of the calcium group of metals among themselves and with lithium nitrate. This has not been quite completed, but there seems to be little doubt from what has been done, that barium nitrate is the most absorbent, that the calcium salt comes next, and that the strontium compound, instead of being intermediate between the others, is less absorbent than either. A series of experiments was also made in which the metal was the same, but the salt radicle varied, the haloid salts of potassium being chosen for this purpose. The bromide and

iodide both absorb enough water to make a solution while the chloride is still in the solid condition, but when the vapour pressure from the bromide and iodide comes to be as great as that of the saturated solution of the chloride, it remains constant until the chloride is all dissolved. Therefore, the three salts absorb nearly the same amounts of water, and it appears that these salts are very nearly equally dissociated, even in rather concentrated solutions, but if anything, the bromide is more dissociated than the others.

Experiments on the resistance of the solutions showed that the amount of dissociation of calcium nitrate is about 45 per cent. as great in a concentrated as in a dilute solution, whilst the amount of dissociation in the case of the lithium salt is about 83 per cent.

H. C.

Determination of the Molecular Weights of some Inorganic Substances. By HEINRICH BILZ (*Chem. Centr.*, 1895, i, 770—771; from *Math. natw. Mitt. Berlin*, 1895, 35—38).—The author has determined the density of some of the elements at a very high temperature by means of an apparatus made of a highly refractory porcelain. The experiments with arsenic, thallium, cadmium, and zinc were made at 1732—1748°. The density of arsenic vapour was found to be 5.30—5.54, the theory for As_2 being 5.2. The dissociation at this high temperature was not greater in hydrogen than in nitrogen. Thallium showed a density of 14.77, theory for Tl_2 requiring 14.11. Cadmium had a density of 4.34—4.38, theory requiring 3.87 for Cd. Zinc had a density of 2.64, theory requiring 2.25 for Zn. Iridium and tin did not evaporate at these high temperatures.

Arsenic trioxide has, between 500—770°, a density corresponding with the formula As_4O_6 . The same diminishes with a higher temperature, and has, at 1732°, the value 7.32, theory for As_2O_3 requiring 6.84. It seems that, above 1770°, only molecules of the compound As_2O_3 can exist. The increase in the boiling point of aqueous solutions of both varieties of arsenious anhydride showed that decomposition into 2 mols. of arsenious acid, H_3AsO_3 , had occurred. The solution of the crystallised variety of arsenious anhydride in nitrobenzene seems, on the other hand, to contain unaltered As_4O_6 .

Attempts were made to estimate the vapour density of the alkali metals and of magnesium, but constant values could not be obtained although any action of the metals on the porcelain vessel was prevented.

L. DE K.

Specific Volume and the Genesis of the Elements. By CHARLES T. BLANSHARD (*Chem. News*, 1895, 72, 230—231, 237—238).—Continuing his observations in reference to the genesis of the elements (Abstr., 1895, ii, 340), the author now points out that the specific volumes in certain homologous series of organic compounds offer parallels to various conditions that obtain with the atomic volumes of series of related elements.

D. A. L.

Molecular Volumes. By ISIDOR TRAUBE (*Ber.*, 1895, 28, 2722—2728; compare Abstr., 1895, ii, 209).—The author compares the observed and calculated values (Abstr., 1895, ii, 70) of the molecular

solution volumes of a large number of organic compounds of very different types, and finds a very close agreement between them; he gives a revised table of atomic solution volumes for the non-metallic elements, and states that the molecular contraction volume per gram-molecule of substance dissolved in water should be 13.5 c.c. instead of 12.2 as previously given. The molecular solution volume is not a purely additive property, but a highly constitutive one, the atomic solution volumes for the various types of oxygen, carbon, nitrogen, sulphur, &c., in organic compounds having very different values; the presence of a benzene or hexamethylene ring in the molecule decreases the molecular solution volume of the compound by 8.1 c.c. The molecular solution volume is not simply the sum of the atomic solution volumes of the atoms forming the molecule, as an expansion always occurs during the formation of a substance; this "molecular dilatation" is approximately the same for all substances, and is 12.4 c.c. per gram molecular weight for the gram molecular volume in aqueous solution at 15°; to obtain the molecular volume this number 12.4 must naturally be increased by the addition of 13.5 c.c.; the molecular contraction volume for water thus becomes 25.9 c.c.

W. J. P.

Molecular Volumetric Determination of Molecular Weights.

By ISIDOR TRAUBE (*Ber.*, 1895, **28**, 2728—2730; compare preceding abstract).—From a single specific gravity determination of an aqueous solution containing 0.5—3 per cent. of a substance, the molecular solution volume of the latter can be calculated, and a correct molecular weight assigned to the substance, using the equation (*Abstr.*, 1895, ii, 70)—

$$v_m = m + aq/d - aq/\delta = \Sigma nC + 12.4.$$

The influence of ionic dissociation and of the presence of the various types of ring present in the substance must, of course, be taken into consideration.

In determining the molecular weight of an acid, it is usually convenient to neutralise the solution with standard soda, using phenolphthaleïn as an indicator, and to then determine the molecular solution volume of the sodium salt, which in so dilute a solution is practically wholly dissociated. The molecular solution volume of sodium metamidobenzoate determined in a 3.030 per cent. aqueous solution was found to be 89.1 c.c., whilst the calculated value is 89.2 c.c.; very accurate results may therefore be obtained.

W. J. P.

Molecular-volumetric Method of Determining the Molecular Weight and Constitution. By ISIDOR TRAUBE (*Ber.*, 1895, **28**, 2924—2928).—The author gives the following formula for calculating the molecular volumes of the hydrocarbons at 15°.

$$V_m = \Sigma nC + 25.9 - (pR + q\equiv + r\equiv),$$

where ΣnC is the sum of the products of the atomic volumes and the number of atoms present, and p , q , r are respectively the number of rings, of double, and of triple linkings. The atomic volume of carbon is 9.9, of hydrogen 3.1, the decrement for each hexamethylene

ring 8.1, for each benzene ring 13.2, for each double linking 1.7, and for each triple linking $2 \times 1.7 = 3.4$. The molecular volumes of 80 hydrocarbons calculated by this formula are given in the paper and compared with those obtained directly from the specific gravities. The agreement between the two series is excellent, and in no case is a greater difference than 6.3 c.c. observed. Since doubling the molecular weight would cause a difference of 25.9 c.c., the application of the method to the determination of molecular weights is evident (compare Abstr., 1895, ii, 209). H. C.

Initial Rates of Osmosis of certain Substances in Water and in Liquids containing Albumin. By W. S. LAZARUS-BARLOW (*J. Physiol.*, 1895, 19, 140—166).—See this vol., ii, 196.

Correct Formulæ for Osmotic Pressure, Changes of Solubility, Freezing Point and Boiling Point; and Heats of Solution and Dilution in Dissolved Dissociated Substances. By J. J. VAN LAAR. II. (*Zeit. physikal. Chem.*, 1895, 18, 245—282).—The author investigates, thermodynamically, the above formulæ, and obtains theoretically the following results. If a strongly dissociated compound is added to a dilute solution of a feebly dissociated substance with one common ion, the dissociation degree of the former remains almost unaltered, that of the latter compound being diminished. When also there is one ion common, the solubility of the compound is lowered, the least soluble undergoing the greatest relative change. Non-electrolytes do not affect the solubility, neither are they affected in this respect. When there is no common ion, the effects are more complicated, and frequently undetermined. In the case of partition coefficients between water and other solvents, it is seen that, owing to the ions being absent in the other solvents, the apparent partition coefficient increases with dilution. The effect of association of the solvent molecules on the formulæ deduced here and in the former paper (1895, ii, 107) is considered, and, where necessary, alterations for this given. It is also shown that the vapour pressure of water is not influenced by the presence of indifferent gases, and that the validity of Dalton's law is limited to the cases where the volume is great. L. M. J.

The Absorption of Nitrous Oxide in Water and in Salt Solutions. By VICTOR GORDON (*Zeit. physikal. Chem.*, 1895, 18, 1—16).—The author has determined the absorption coefficient of nitrous oxide in solutions of chlorides of potassium, sodium, lithium, calcium and strontium, and sulphates of potassium, sodium, lithium, and magnesium. The experiments were in each case performed for three or more concentrations, and at five different temperatures, ranging from 8.1° to 22.3°, and interpolation formulæ* are given for each solution examined. The lowering of the absorption coefficient appears to be proportional to $M^{\frac{1}{2}}$, where M is the number of gram

* It is noticeable that these interpolation formulæ are in all cases of the form $a = a - \beta t + \gamma t^2$ indicating, if the formula holds for extrapolation, a minimum at the temperature $\beta/2\gamma$, which in almost all cases lies between 34° and 40°.

molecules of dissolved salt per litre, so that $(a-a_s)/M^{\frac{1}{2}} = \text{const.}$, a and a_s being the coefficient in water and the solution respectively. The value of the constant decreases as the temperature rises, and varies with different salts. For analogous salts, however, the constants are nearly equal, whilst the value for bivalent salts is double that for univalent salts.

L. M. J.

The Partition Coefficients of Solutions in Liquid and Solid Substances. By JACOBUS M. VAN BEMMELEN (*Zeit. physikal. Chem.*, 1895, **18**, 331—334).—The results and conclusions of G. C. Schmidt (Abstr., 1895, ii, 39) are contested. Neither in silicic acid nor in any other substance experimented with by the author, did he find the absorption took place in accordance with Henry's gaseous law ($c_2/c_1 = \text{const.}$, where c_2 and c_1 are the concentrations of dissolved substance in the liquid and solid respectively). The partition coefficient was in all cases not constant, but a complex function of the concentration, and dependent on the temperature and modification of the colloid. The coefficient is only approximately constant when the concentration is small, so that the author considers Schmidt's conclusions erroneous.

L. M. J.

Note by Abstractor.—The partition coefficient should, however, only be constant when the solid absorbent, that is, the colloid, remains of the same modification, and only for dilute solutions, as in strong solutions Henry's law could not be expected to hold.

Self-recorded Breaks in the Properties of Solutions. By P. SPENCER U. PICKERING (*Phil. Mag.*, [5], **40**, 472—476).—By running a continuous stream of sulphuric acid into water in a calorimeter, and making a chart of the motion of the thermometer, either by photography or by taking successive readings, a diagram is obtained which reproduces automatically the sudden changes of curvature shown by the author's heat of dissolution determinations (*Trans.*, 1890, 127). By adjusting the initial temperature suitably, the figures obtained are rectilinear, and the breaks become as clearly visible as those which are made on starting or stopping the stream of acid.

S. U. P.

Cryoscopic Relations of Dilute Solutions of Cane Sugar and Ethylic Alcohol. By HARRY C. JONES (*Phil. Mag.*, 1895, [5], **40**, 383—393; and *Zeit. physikal. Chem.*, 1895, **18**, 283—293).—Nernst and Abegg (Abstr., 1895, ii, 155) have attributed the high results obtained by the author for the molecular lowering of the freezing point in dilute cane sugar solutions to the use of a jacket at a much lower temperature than the freezing point of the solution. The experiments have therefore been repeated, using a freezing mixture from 0.3° to 0.4° colder than the freezing point of the solution. A large volume of solution (1100 c.c.) was employed, thus diminishing very greatly the effect of disturbing influences from without. The stirring was carried out so gently that errors from this source could not have assumed any appreciable dimensions. The results obtained are as follows.

Grams in litre.	Normal.	Lowering found.	Gram-mol. lowering.
3·8875	0·01136	0·0251	2·21
7·775	0·0227	0·0475	2·09
15·550	0·0455	0·0915	2·01
23·325	0·0682	0·1333	1·95
31·100	0·0909	0·1734	1·91

The molecular lowerings are throughout somewhat lower than those obtained in former determinations, but they are still far above the theoretical value. Dilute solutions of ethylic alcohol gave similar results, and the author does not find sufficient justification for the conclusion that non-electrolytes in fairly dilute solutions give lowerings which conform to the equation $t = 0\cdot02 T^2/W$. H. C.

Relations between the Cryoscopic Behaviour of the Phenols and their Constitution. By KARL AUWERS (*Ber.*, 1895, 28, 2878—2882).—Although, as the result of former investigations (*Abstr.*, 1894, ii, 133; 1895, ii, 41), the author was led to conclude that the cryoscopic behaviour of the phenols in benzene solution was normal, certain irregularities observed with paracresol and para-nitrophenol rendered this conclusion doubtful. The author has, therefore, submitted this point to the test of further experiment, but, as many of the phenols are only very slightly soluble in benzene at the freezing point, naphthalene has been substituted for benzene as a solvent. Forty-eight phenols were examined in all, namely, phenol and 6 of its homologues, 5 halogen derivatives, 9 nitrophenols, 8 hydroxyaldehydes, 14 phenolcarboxylic acids, and 5 polybasic phenols. The acids were used in the form of their methylic or ethylic salts.

The examination of these substances shows that the cryoscopic behaviour of the phenols is largely dependent on their constitution. Phenols, where substitution is in the ortho-position, exhibit the normal cryoscopic behaviour, but para-substituted phenols behave abnormally. The meta-compounds occupy a position between the ortho- and para-, but rather resemble the para-compounds in their behaviour. Among the substituting groups, the influence of the aldehydic group $\cdot\text{CHO}$ is the most marked, and then in decreasing order of influence follow the carboxalkylic group $\cdot\text{COOR}$, the nitro-group, the halogens, and, lastly, the alkyl groups. The influence of ortho-substitution is stronger than that in the meta- or para-position, so that if a phenol contains the same substituting group in both the ortho- and para-positions, the cryoscopic behaviour of the substance will probably be nearly normal. No exceptions to the above regularities have as yet been met with, and it is suggested that the cryoscopic behaviour of a phenol may aid materially in the determination of its constitution.

H. C.

Cryoscopic Behaviour of Substances having Constitutions similar to that of the Solvent. By EMANUELE PATERNÒ (*Gazzetta*, 1895, 25, i, 411—417).—Garelli and Montanari (*Abstr.*, 1895, ii, 205) showed that the phenols when dissolved in the corresponding hydrocarbons give abnormal depressions of the freezing points, and conclude that this is due to the close chemical relationship existing between

the solvent and the dissolved substance; the author shows, however, that this similarity of constitution is not the only cause of a small depression of the freezing point, but that the chemical nature of the dissolved substance has also to be considered. Thus, phenol behaves abnormally, whether dissolved in benzene or in paraxylene; paraxyleneol also gives abnormal freezing point depressions both in paraxylene and benzene solutions; the similarity of constitution of the solvent and dissolved substance seems in these cases to be without effect. Determinations of the depression in freezing point caused by phenol and benzylphenol in diphenylmethane solution show that phenol behaves fairly normally and benzylphenol quite abnormally, as would be expected from Garelli and Montanari's conclusion.

W. J. P.

Freezing of Solutions at Constant Temperature. By ALBERT COLSON (*Compt. rend.*, 1895, **120**, 991—993).—An increase of pressure raises the freezing points of liquids which contract during solidification, whilst, on the other hand, the presence of dissolved foreign matter lowers the freezing point in inverse proportion to the molecular weight of the dissolved substance. The author has endeavoured to ascertain experimentally whether any relation exists between the molecular weight of the dissolved substance and the pressure required to maintain the freezing point of the solvent constant. The solvent selected was benzene freezing at 5.7° . The results are given in the following table.

Dissolved substance.	M.	p .	t .	P.
Benzoic acid	122	2.5	0.53°	98 mm.
Acetic acid.....	60	2.5	1.16	232 „
Naphthalene.....	128	2.5	1.06	219 „
Paradichlorobenzene..	137	2.5	0.92	180 „
Paradichlorobenzene..	137	5.0	1.85	410 „
Metadinitrobenzene ..	168	3.0	0.98	225 „

Here M is the molecular weight of the dissolved substance, p the number of grams dissolved in 100 grams of benzene, t the depression of the freezing point, and P the pressure in mm. in Amagat's apparatus required to raise the freezing point of the solution to that of the solvent (5 mm. on this scale correspond with about 1 atmos.). It will be seen that in the case of benzoic and acetic acids there is no direct relationship between the pressures corresponding with a particular freezing point depression and the molecular weights of the acids. On the other hand, if we consider three of the solutions in which the depression of the freezing point is about 1° , we find that the pressure which may be regarded as equivalent to a depression of 1° is in each case about the same, thus: acetic acid, $232/1.16 = 200$; naphthalene, $219/1.06 = 206$; chlorobenzene, $180/0.92 = 194$.

H. C.

Influence of Chemical Constitution of Organic Compounds on their capability of forming Solid Solutions. By FELICE GARELLI (*Zeit. physikal. Chem.*, 1895, **18**, 51—60).—The paper contains further examples of abnormal depressions of the freezing point occurring when solvent and dissolved substance are closely

allied in constitution. Cumarone, indole, and indene in naphthalene give too high values for the molecular weight, as do diphenylene oxide and β -naphthoquinoline in phenanthrene, phenanthroline in the same solvent giving a normal result. Dithienyl gives an abnormal depression in diphenyl, but normal in benzene, whilst metanicotine gives a normal value in diphenyl, a result in accord with the views of Pinner (Abstr., 1894, i, 388; 1895, i, 116). The regularity observed in the cyclic compounds is markedly modified by the presence of side chains, thus methylpyrroline gives a normal depression in benzene, as do pyrroline and thiophen in paraxylene, whilst $\alpha\alpha$ -dimethylpyrroline and $\alpha\alpha$ -dimethylthiophen give abnormal values in paraxylene. In acetophenone, acetylpyrroline and acetothienone give, as expected, abnormal depressions. In benzoic acid as solvent, α -pyrrolinecarboxylic acid, α -thiophencarboxylic acid, ortho- and meta-hydroxybenzoic acids, and orthamidobenzoic acid give abnormal depressions, whilst those caused by parahydroxybenzoic and furfuran-carboxylic acids are normal, those due to meta- and para-amidobenzoic acids being nearly so. In phenol, the three dihydroxybenzenes are slightly abnormal, whilst in resorcinol the ortho- and para-compounds give normal values. Some fatty compounds are also examined: maleic anhydride in succinic anhydride giving an abnormal result, whilst those of oleic acid in stearic acid, butyric acid in crotonic acid, apirole and dihydro-apirole in isapirole are normal. In a short note on Beckmann's work (Abstr., 1895, ii, 383), the author does not consider that the abnormal results of iodine in benzene solution can be due to the formation of a solid solution.

L. M. J.

The Velocity Law of Polymolecular Reactions. By ARTHUR A. NOYES (and WALTER O. SCOTT) (*Zeit. physikal. Chem.*, 1895, **18**, 118—132).—For the determination of the order of a chemical reaction, the constancy of the velocity constant is not alone sufficient, but comparison should be made of the constants, at a definite stage of the action, obtained in independent experiments with different initial concentrations. Examined thus, it is seen that the action between hydrogen iodide and hydrogen peroxide is of the second order (see Magnanini, Abstr., 1892, 110), whilst the same holds for the action between hydrogen iodide and bromic acid. According to Schwicker's experiments (Abstr., 1895, ii, 213), the decomposition of potassium hypoiodite is, if in the presence of free iodine, of the first order, but no definite conclusion can be drawn if alkali is in excess. The reaction between ferric and stannous chlorides is, however, of the third order, as is the polymerisation of cyanic acid. An explanation of the first three cases, may be that the reaction takes place in two or more stages, of which the first alone takes an appreciable time. For example, $\text{HI} + \text{H}_2\text{O}_2 = \text{HIO} + \text{H}_2\text{O}$; $\text{HIO} + \text{HI} = \text{H}_2\text{O} + \text{I}_2$. In the last two cases, van't Hoff's law, that the order is determined by the number of interacting molecules, is obeyed.

L. M. J.

A Reversible Reaction of the First Order. By FRITZ W. KÜSTER (*Zeit. physikal. Chem.*, 1895, **18**, 161—179).—The reversible

change of hexachlor- α -keto- β -pentene \rightleftharpoons hexachlor- α -keto- γ -pentene is considered. The estimation of the compounds is effected readily, owing to the slight solubility of the anilide of the β -compound. The β -compound was heated at 210° , and the quantity of the γ -compound estimated hourly, the final state being reached when the quantity was 0.386, whilst the value of $1/t \log 1/(1 + c'/c)x$ varied from 0.055 to 0.035. The change from the γ -compound to the β - was examined at the same temperature, the final stage being reached when 0.613 of the β -compound was formed, a number agreeing exactly with the previous results. Experiments in different atmospheres showed that small quantities of aqueous vapour have a high accelerative influence, the same obtaining to a smaller extent for hydrogen chloride. An increase in temperature to 237.5° caused the velocity to increase tenfold, but the final ratio was only slightly altered, 0.63 to 0.65. At 300° , equilibrium was very speedily reached, the final ratio being 0.85.

L. M. J.

Velocity of the Hydrolysis of Salicin by Acids. By ARTHUR A. NOYES and WILLIAM J. HALL (*Zeit. physikal. Chem.*, 1895, **18**, 240—244).—The investigations were undertaken to determine whether the hydrolysis of a glucoside is in accordance with the reaction law which obtains for the inversion of cane sugar, &c. Salicin was employed for the purpose, the formation of either saligenin or saliretin during the reaction being immaterial, as both are inactive. A 5 per cent. solution was first employed, the rotation of which was -12.32° , and when completely hydrolysed $+6.00^\circ$, the ratio being hence $0.487 = c$. If the reaction takes place according to the equation $dx/dt = k(A - x)$, the value for the constant k is given by $1/t \log \{(ca_0 + a_1)/(ca_0 + a)\}$, where a_0 is the initial rotation, a_1 that at the arbitrary zero of time, and a that after time t . The values thus obtained for k are in close accord, the greatest variation being about 8 per cent., and the reaction therefore, like the sugar inversion, is of the first order. The relative effects of the acids follow the same order as their effects in sugar inversion, as is seen in the following table.

N/5 acid.	Salicin hydrolysis.	Sugar inversion.
Hydrochloric.....	1000	1000
Sulphuric.....	499	536
Oxalic.....	223	186
Malonic.....	45	31

L. M. J.

Molecular Symmetry and Asymmetry. By PAUL GROTH (*Ber.*, 1895, **28**, 2510—2511).—The generally accepted statement, contradicted by Ladenburg (*Abstr.*, 1895, ii, 489), that when the molecule of a substance contains no plane of symmetry, the substance exhibits enantiomorphism, is quite correct, for planes of symmetry are of two kinds, namely, simple and compound. A figure possesses a plane of simple or direct symmetry when it gives a superposable image on

reflection from that plane, whilst it possesses a plane of compound or indirect symmetry when a superposable image is only obtained after reflection and rotation through 180° about the normal to the plane. Diketopiperazine, the example quoted by Ladenburg, possesses a plane of compound symmetry, and, therefore, cannot exhibit enantiomorphism; the application of the term pseudosymmetry to such a case is undesirable, this term being already used in another way.

The author points out that the whole question of the symmetry of geometrical figures is now worked out in crystallographic text-books in such a way as to be immediately applicable to all problems concerning molecular symmetry.

W. J. P.

Size of Crystalline Molecules. By ANDREAS FOCK (*Ber.*, 1895, 28, 2734—2742).—Nernst has shown (*Abstr.*, 1892, 560) that when an aqueous solution, containing c_1 and c_2 molecules of two isomorphous salts per unit volume, is in equilibrium with a solid solution composed of x_1 and x_2 molecules per cent. of the same two salts respectively, the ratios c_1/x_1 and c_2/x_2 are constant for all concentrations if the molecular weights of the two salts are the same in both the liquid and the solid solutions; if, however, the molecular weight in the solid state is n times that in the liquid state, n being greater or less than unity, then c_1^n/x_1 and c_2^n/x_2 are constant. If ionic dissociation occurs, the number of molecules in the liquid solution changes, and this alteration must be allowed for in using the above constants; but inasmuch as the extent of the electrolytic dissociation of two salts having a common ion, in aqueous solution, is the same, the above ratio should remain practically constant when the solubility of the two salts in molecules per unit volume is nearly the same; if the dissociation is slight, it can of course also be disregarded.

Disregarding dissociation, therefore, the author has calculated the values of the above ratios taking the pairs of isomorphous salts investigated by Muthmann and Kuntze (*Abstr.*, 1895, ii, 7) and shows that potassium dihydrogen phosphate and arsenate have the same molecular weight both in solution and in the crystalline state. Potassium permanganate and perchlorate and rubidium permanganate have, however, twice the molecular weight when solid that they have when liquid.

The author contends that Muthmann and Kuntze's numbers for the equilibrium between potassium and rubidium permanganates and their aqueous solution show that the two salts crystallise together in all proportions, and not between very narrow limits as stated in the paper quoted above.

W. J. P.

Running together and Healing of Crystals. By OTHO LEHMANN (*Zeit. physikal. Chem.*, 1895, 18, 91—96).—On warming potassium oleate, or even ordinary soap, on a microscope slide with insufficient alcohol for its complete solution, and allowing the slide to cool, pointed tetragonal octahedra separate; these crystals are 0.1—0.3 mm. in length and each usually consists of a string of several individual crystals; they are best observed by using alcohol coloured red by

some dye which is not taken up by the deposited crystals. When, by moving the cover-slip two of these crystals are so brought into contact that their long diameters become perpendicular, or in approximately the position of twinning, the sharp end of the one crystal merely flattens itself against the mass of the other; if, however, by manipulating the cover slip, the crystals be moved until their longer axes are at about 60° , the smaller crystal turns of its own accord until in a parallel position to the larger one, and then the two crystals so join together as to form one homogeneous whole. The tendency which deformed soft crystals, such as these, have, towards again assuming a regular form, may be also observed by crushing one of the larger crystals of potassium oleate into small detached fragments by pressure on the cover slip; the small fragments soon become of quite symmetrical form.

The processes involved in these changes are obviously the same as those by which a broken crystal becomes whole, or heals itself when immersed in its crystallising solution; in the latter case, the surface tension of the solid mass can only act through the agency of the solution, whilst with soft crystals like the above, the surface tension of the solid is sufficiently powerful to cause the arrangement of the fragments in parallel orientation.

W. J. P.

Convenient Forms of Laboratory Apparatus. By D. ALBERT KREIDER (*Amer. J. Sci.*, 1895, [3], 50, 132—134).—The author describes a simple form of *hot filter*. The jacket consists of an inverted flask, the bottom of which has been removed, the top of the funnel fits into this opening, and the neck is closed by a stopper containing perforations for the stem of the funnel, and for the steam and waste pipes. An improved form of the ordinary *Bunsen valve* is also described. It consists of a stout glass tube sealed at one end and drawn out in the middle with an opening in the constriction, a piece of rubber tubing containing a smooth slit is placed over this. The collapse of the rubber, which is so common in the Bunsen valve, is thus rendered impossible. The valve works much better when lubricated with glycerol. A convenient *force pump* may be constructed by adjusting two of the valves just described to the opposite extremities of a T-tube, whilst the third limb is enlarged so as to permit the attachment of a large and stout piece of rubber tubing closed at one end; this tube being alternately compressed and released by the hand.

J. J. S.

A New Refractometer. By CARL PULFRICH (*Zeit. physikal. Chem.*, 1895, 18, 294—299).—The author has devised some improvements on the older form of his well-known refractometer so that the instrument is now available for the determination of the refractive index and dispersion not only for sodium light, but also for the C, F, and G lines. A heating arrangement is also added for the investigation of liquids at various temperatures, and of compounds which have high melting points, whilst the new instrument is also adapted for use as a differential refractometer—that is for the direct determination of the refractive index or dispersion of one solid or liquid with respect to a second.

L. M. J.

Inorganic Chemistry.

Possibility of the Occurrence of Hydrogen and of Methane in the Atmosphere. By FRANCIS C. PHILLIPS (*J. Amer. Chem. Soc.*, 1895, **17**, 801—809).—Since hydrogen and methane are largely evolved during the decay of organic matter under water, and since, by the gradual erosion of rocks, quantities of natural gas are being constantly liberated, the author thinks it is quite probable that both these gases may exist in the atmosphere. Experiments made at Mount Washington, New Hampshire (7,000 ft. above sea level) gave negative results, but it is suggested that experiments should be made at much greater altitudes, as, since hydrogen and methane are both very light, they would tend to form a zone resting on the heavier gases of the atmosphere.

The author recommends the use of anhydrous palladium chloride for the detection of traces of hydrogen in a mixture of gases. Free hydrogen reduces this salt in the cold, forming hydrogen chloride, which can be tested for by means of silver nitrate. J. J. S.

Combination of Hydrogen with Oxygen. By VICTOR MEYER and WILHELM RAUM (*Ber.*, 1895, **28**, 2804—2807).—When heated in sealed bulbs for 10 days, at 300°, hydrogen and oxygen do not appear to combine at all, but when the heating is continued at the same temperature for 65 days (300—305°) the amounts of water formed in three bulbs were 9·5 per cent., 0·4 per cent., and 1·3 per cent. When heated at 100° even for 218 days and nights, no water appears to be formed. The authors consider that these experiments confirm the theoretical view that combination actually takes place between hydrogen and oxygen at the ordinary temperature, but at so slow a rate that no appreciable amount of water is formed during a measurable period. A. H.

Hydrogen Peroxide. By JULIUS W. BRÜHL (*Ber.*, 1895, **28**, 2847—2866).—A detailed historical account of the discovery and investigation of hydrogen peroxide is given. The specimens employed were prepared by distilling under diminished pressure the commercial article after the addition, if necessary, of a little barium hydroxide to remove silicic acid and salts of the heavy metals; the purest preparation boiled at 69·2° (26 mm.). The stability increases with the concentration, specimens containing 95—100 per cent. H_2O_2 are scarcely changed after 5—7 weeks, if direct sunlight is excluded, the surface reduced as much as possible, and the containing vessel kept smooth; prolonged shaking favours decomposition, and the compound cannot be conveniently transported by train. Guncotton is the best medium for the filtration of hydrogen peroxide, asbestos causes rapid decomposition, and wool readily ignites. Surface action is entirely excluded if the vessel is coated with paraffin; the optical constants given below

were determined with prisms treated in this manner, as ground glass causes immediate decomposition of the hydrogen peroxide.

If the hydrogen peroxide is isolated by the help of ether, great care is required during the distillation; on one occasion, a specimen prepared in this manner smelt strongly of ozone, an oily substance remained which did not volatilise at 100° , had no smell, and detonated feebly when a drop was placed on platinum in a flame, but the introduction into it of a sharp-edged, glass rod caused a violent and disastrous explosion.

The sp. gr. is 1.4584 at $0^{\circ}/4^{\circ}$, and 1.4378 at $20^{\circ}/4^{\circ}$. Four series of determinations of the optical constants were made, of which the following values, for the molecular refraction and dispersion, are regarded as the most accurate. $M_a = 5.791$; $M_{Na} = 5.817$; $M_{\gamma} - M_a = 0.136$, the calculated values for the formula $HO \cdot OH = 5.18, 5.32$, and 0.10 respectively. The corresponding values for oxygen are as follows.

	M_a .	M_{Na} .	$M_{\gamma} - M_a$.
Oxygen in water (20).....	2.968	3.212	0.036
„ hydrogen peroxide..	3.591	3.717	0.055
„ molecular O_2 , liquid.	3.958	3.964	0.069
„ „ gaseous	—	4.09	—

This increase in the values of molecular oxygen probably denotes the presence in it of one or more double linkings, and, from its analogy to sulphur, oxygen is probably quadrivalent. In support of this view, the compounds Ag_2O and $HClOMe_2$ are cited; the latter is known both as gas and liquid; the formation of hydrogen peroxide from nascent hydrogen and molecular oxygen, its decomposition by means of nascent oxygen, and its resolution into water and molecular oxygen are also mentioned. Reference is made to the optical constants of carbonic oxide, which have been shown by the author to be higher than those calculated from the formula $C:O$; this compound he regards as $C:O$, all other organic oxygen compounds being "unsaturated" in the same sense as bivalent sulphur derivatives, and compounds of trivalent phosphorus and nitrogen (compare Tafel, Abstr., 1894, ii, 448). J. B. T.

Constitution of Water and the Cause of its Dissociating Power. By JULIUS W. BRÜHL (*Ber.*, 1895, **28**, 2866—2868; and *Zeit. physikal. Chem.*, 1895, **18**, 514—518).—Assuming the quadrivalency of oxygen (compare preceding abstract), water must be an unsaturated compound; to this cause is referred its great dissociating power both for molecular aggregates and single molecules, its readiness in combining with other substances, and the ease with which it forms molecular aggregates. The fact that most substances are more or less hygroscopic and soluble in water is cited in further proof. The organic compounds which most closely resemble water in these properties, such as the alcohols, ketones, ethereal salts, acids, &c., also contain oxygen, and their dissociating power generally decreases as the molecular weight rises and the content of oxygen falls. The hydrocarbons and their haloïd substitution products have little or no dissociating power. J. B. T.

Separation of Tellurium from Copper Residues. By CABELL WHITEHEAD (*J. Amer. Chem. Soc.*, 1895, **17**, 849—855).—All copper produced from American sulphide ores contains tellurium. A method for the estimation of this tellurium has already been given (*Abstr.*, 1895, ii, 289). In the electrical refining of copper, the washings from the gold residues contain the tellurium as tellurous oxide or sulphate. The tellurium may be obtained from these either by precipitation with copper or by passing sulphurous anhydride through the solution. It may be finally purified by distillation in hydrogen.

When a solution of sodium tellurite is added to a solution of an ammonium salt, a white precipitate of tellurous anhydride is thrown down, which becomes granular on boiling. A small amount of tellurium or of some metal which can be precipitated by sulphurous anhydride remains in solution; this soluble portion is still under investigation. Potassium ferrocyanide does not react with tellurium chloride at once, but, after a few hours, Prussian blue is formed.

When tellurium is heated with aluminium, the two combine with explosive violence, forming a chocolate coloured, difficultly fusible compound, which has the composition Al_2Te_3 . It is hard and brittle, and can readily be ground to powder; when exposed to moist air, it is decomposed, and hydrogen telluride is slowly evolved; when thrown into water, it is rapidly decomposed.

Tellurium is readily deposited by an electric current either from an acid or alkaline solution. It has been found possible to separate tellurium from copper by adding an excess of sodium hydroxide and about 3 grams of potassium cyanide for each gram of copper present, and passing an electric current through the solution; when the tellurium is thrown down as a black, non-adherent precipitate, which can readily be filtered off; the solution can then be slightly acidified with sulphuric acid and the copper estimated in the usual way by electrolysis.

J. J. S.

Action of Gaseous Hydrogen Chloride on Salts of the Elements of the Fifth Group of the Periodic System. By EDGAR F. SMITH and JOSEPH G. HIBBS (*J. Amer. Chem. Soc.*, 1895, **17**, 682—686).—The authors find that sodium nitrate, when heated in a current of hydrogen chloride, is completely converted into sodium chloride. Phosphates are not decomposed, in so far that no phosphorus chloride is given off; but arsenates of sodium, magnesium, and lead are completely converted into chlorides, whilst the arsenic is entirely volatilised (as chloride or ? oxychloride), and may be collected in a bulb apparatus filled with water. When acting on sodium vanadate, the vanadium is expelled as oxychloride.

L. DE K.

Action of Gaseous Halogen acids on the Salts of the Elements of the Fifth Group of the Periodic System. By EDGAR F. SMITH and FRED L. MEYER (*J. Amer. Chem. Soc.*, 1895, **17**, 735—739).—Sodium nitrate is completely converted into the corresponding fluoride by the action of hydrogen fluoride at 250° . Phosphates are not attacked. Vanadates are but partially decomposed, and even at a

high temperature only about one-half of the vanadium is expelled. The same result was obtained with arsenates.

When working with hydrogen bromide, it is found that sodium nitrate is completely converted into the corresponding bromide. Phosphates are not acted on. Sodium vanadate is strongly, but not completely, attacked with formation of vanadium oxybromide. Arsenates are completely decomposed, all the arsenic being volatilised as bromide.

Using hydrogen iodide, the experiment with sodium nitrate could not be brought to a satisfactory conclusion, owing to the formation of some explosive bye-products. Phosphates are not acted on. Arsenates are, no doubt, completely decomposed, but exact proof is wanting, as explosive compounds are also formed and interfere with a correct analysis.

The action of the gaseous halogen acids on antimony, columbium, and tantalum is also mentioned, but no analytical details are given.

L. DE K.

Data for the Ascertainment of the True Atomic Weight of Carbon. By J. ALFRED WANKLYN (*Chem. News*, 1895, **72**, 164—165).—Arguments are adduced in favour of a reversion to 6 for the atomic weight of carbon (compare this vol., i, 1, 2). Reasons are also assigned for doubting whether Schorlemmer's hydride of heptyl (this *Journal*, 1863, 216) was not a mixture of hydrocarbons.

D. A. L.

Varieties of Graphite. By HENRI MOISSAN (*Compt. rend.*, 1895, **121**, 540—542).—The author has examined specimens of graphite from various localities, mainly with a view of ascertaining which are intumescent, like the graphite obtained by dissolving carbon in metals at very high temperatures, and which are non-intumescent, like the graphite produced by the effect of a high temperature alone on any other form of carbon. *Ceylon*, intumescent; after purification by treatment with fused potash and with hydrofluoric acid, it contains no form of carbon but graphite. *Ticonderoga*, intumescent. *Greenville*, intumescent. *Borrowdale*, non-intumescent, but decrepitates when heated, and gives off about four times its own volume of gas, consisting mainly of hydrocarbons and hydrogen mixed with some air. *Omnesack* (Greenland), crystalline, but non-intumescent. *Mugrau* (Bohemia), and *Scharzbach* (Bohemia), also crystalline but non-intumescent. *Australia*, non-crystalline and non-intumescent.

C. H. B.

Helium and its Place in the Natural Classification of Elementary Substances. By HENRY WILDE (*Phil. Mag.*, 1895, [5], **40**, 466—471).—The author has examined the spectrum of helium obtained by the distillation method from Norwegian clèveite, pitchblende, and other minerals containing uranium, more especially some heavy, zirconiferous sand, containing uranium, which is found in large deposits on the coast of Brazil, and which is a relatively abundant source of helium. The result of these experiments confirms the author's previous conclusion, that the differences in the determinations by different observers of the wave-lengths of the components of the characteristic yellow line, are due to the influence of pressure and

diffusion with other gases in varying the width of spectral lines on the more refrangible side of the spectrum. This shows that, within certain limits, the distance between the components of D_3 is not to be taken as the criterion of the identity of chromospheric and terrestrial helium.

In the author's classification of elementary substances in multiple proportions of their atomic weights, each series or family is considered to be condensations of the typical elements H, H_2 , H_3 , H_4 , H_5 , H_6 , H_7 (*Chem. News*, **38**, 66, 96, 107). The properties of helium indicate that it is the typical element H_3 at the head of the uneven series H_{3n} .

H. C.

Estimation of Argon. By TH. SCHLÆSING, jun. (*Compt. rend.*, 1895, **121**, 604—606).—Further experiments have shown that the error in the estimation of argon by the author's method (this vol., ii, 219) amounts to about 0·7 per cent. of the argon to be estimated, and is not due to any action of the steel, porcelain, asbestos, copper, or cupric oxide on the argon. When the magnesium is not heated, the loss is about 0·25 per cent., and when it is heated, the loss is from 0·5 to 1·0 per cent., and increases with the duration of the experiment and the pressure of the argon in the apparatus.

The following estimations were made with the air of Paris collected 10 metres above the soil.

	Sep. 25.	Sep. 26.	Sep. 30.	Oct. 1.	Oct. 4.	Mean.
Per 100 vols. of air	0·9369	0·9349	0·9367	0·9325	0·9363	0·935
Per 100 vols. of nitrogen	1·185	1·183	1·185	1·180	1·185	1·184

Other estimations were as follows.

	Per 100 vols. of air.	Per 100 vols. of nitrogen.
Air in Normandy at a height of 305 metres..	0·9343	1·182
Air round the Eiffel Tower at a height of 300 metres.....	0·9328	1·180
Air in the gallery of an iron mine.....	0·9354	1·183
	<hr/> 0·934	<hr/> 1·182

The differences are of the same order as the errors of experiment, and it would seem that the proportion of argon in the atmosphere is as constant as that of oxygen or nitrogen. Making the correction of 0·7 per cent. as above, the numbers for normal air become 0·941 and 1·192. Calculation of the difference in density between pure nitrogen and atmospheric nitrogen mixed with argon gives 0·0063, whilst Rayleigh and Ramsay found 0·0067.

The following estimations were made in the gas drawn from various soils.

	Argon per 100 vols. of nitrogen.
At a depth of 0·20 mm. in the soil of a pine wood ...	1·170
„ „ 0·40 „ „ of an arable field..	1·169
„ „ 0·40 „ „ of an arable field..	1·155
„ „ 0·40 „ very light garden soil....	1·118

The lower proportion of argon is probably due to the fact that it is considerably more soluble in water than nitrogen is. C. H. B.

Solubility of Silver Halogen Salts in various Solvents. By ERNST COHEN (*Zeit. physikal. Chem.*, 1895, **18**, 61—69).—The experiments of Valenta (*Abstr.*, 1894, ii, 418) on the solubility of the silver salts of halogen acids in sodium thiosulphate and in potassium cyanide, indicate that the solubility is not that deducible from the equations (I) $3\text{Na}_2\text{S}_2\text{O}_3 + 2\text{AgCl} = (\text{AgS}_2\text{O}_3\text{Na})_2, \text{Na}_2\text{S}_2\text{O}_3 + 2\text{NaCl}$ and (II) $2\text{KCN} + \text{AgCl} = \text{KAg}(\text{CN})_2 + \text{KCl}$. The author has, therefore, examined these solubility phenomena with the following results. (1) Silver chloride, if not in excess, dissolves in sodium thiosulphate in accordance with equation I. (2) If the silver chloride is in excess, the less soluble salt, $(\text{AgS}_2\text{O}_3\text{Na})_2$, is formed. (3) If not in excess, silver chloride dissolves in potassium cyanide solution in accordance with equation II. (4) Excess of the silver salt causes the double salt to be partly decomposed, with formation of silver cyanide and potassium which can react in the reverse sense until equilibrium is reached, $\text{KAg}(\text{CN})_2 + \text{AgCl} \rightleftharpoons 2\text{AgCN} + \text{KCl}$. Valenta's results were due to the fact that he operated with a large excess of the silver haloid L. M. J.

Preparation of Lime and Strontia Crystals. By G. BRÜGELMANN (*Zeit. anorg. Chem.*, 1895, **10**, 415—433).—The author has already shown that the alkaline earths can be obtained in crystals by melting and decomposing their nitrates by means of heat. The conditions necessary for the formation of good crystals are that the crucible be heated to the necessary temperature only on one side; that perfectly dry calcinum nitrate be employed, and that the crucible be tightly covered during the decomposition so that the air and furnace gases are excluded. Crystals of lime, measuring 1.6 cm., and of strontia, 5.5 mm. in length, have been obtained. A complete description, with drawings, of the furnaces employed, is given in the original paper. The lime crystals are prepared in porcelain crucibles, the strontia crystals in platinum crucibles. The crystals must be carefully preserved in air-tight vessels, dried with pieces of lime and strontia. On exposure to air, they turn dull, but may be brought to their former brightness by heating with dry lime or strontia.

E. C. R.

Normal Calcium Chromite. By E. DUFAU (*Compt. rend.*, 1895, **121**, 689—691).—A mixture of 115 grams of chromic oxide and 45 grams of calcium oxide was heated in the electric furnace with a current of 700 amperes and 50 volts. The product is a mixture of yellow lamellæ, similar to those obtained by Moissan by heating chromium and calcium oxides in the electric arc, and green, acicular crystals, which are found in the hottest parts of the furnace, and are, therefore, stable at high temperatures. The product is heated with boiling, concentrated, hydrochloric acid until nothing more dissolves. The residue consists of lustrous green, prismatic needles of the normal chromite, $\text{CaO}, \text{Cr}_2\text{O}_3$; sp. gr. = 4.8 at 18°; hardness about 6°. The crystals are not attacked by fluorine in the cold, but on gently

heating an energetic action takes place with incandescence. Chlorine attacks the chromite slowly at a bright red heat, but bromine, iodine, and sulphur are without action at the softening point of glass, and water vapour has no effect at a bright red heat. At the softening point of glass, the chromite burns brilliantly in oxygen, with formation of calcium chromate and chromic oxide. Hydrofluoric and hydrochloric acids and concentrated nitric and sulphuric acids have no action on the chromite, but dry, gaseous hydrogen fluoride and hydrogen chloride decompose it at a red heat. Fused potassium nitrate or chlorate or hydroxide, or fused alkali carbonates readily attack the chromite.

In composition, the chromite is identical with that obtained by Gerber by heating calcium chloride with potassium dichromate.

C. H. B.

Preparation of Pure Beryllium Oxide from Emerald. By PAUL LEBEAU (*Compt. rend.*, 1895, **121**, 641—643).—The emerald is first fused with twice its weight of calcium fluoride in a plumbago crucible by means of a coke fire, and the fused mass is poured into water. A friable product is thus obtained which is very energetically attacked by sulphuric acid, even in the cold. When evolution of silicon fluoride ceases, the residue is strongly heated until sulphuric anhydride is given off freely, and then thrown into water in small quantities at a time. The clear liquid is decanted, concentrated, partially neutralised with potassium carbonate, and allowed to cool, when the greater part of the aluminium separates as alum. An impure beryllium ammonium carbonate is obtained from the mother liquor by treating it with ammonia and ammonium carbonate.

Another plan is to heat the emerald in a carbon tube in the electric furnace; a large quantity of silica is volatilised, and the residue, which contains only about 30 per cent. of silica, breaks up into powder as it cools. This basic silicate is decomposed by acids, and is treated with a mixture of hydrofluoric and sulphuric acids.

The impure beryllium ammonium carbonate is dissolved in nitric acid, the iron precipitated by a small quantity of potassium ferrocyanide, the excess of ferrocyanide removed by means of copper nitrate, and the excess of copper by hydrogen sulphide. The solution is then mixed with ammonia, and the precipitate allowed to remain in the liquid for three or four days, so that the alumina may polymerise and become insoluble in ammonium carbonate. The liquid is then decanted, and the precipitate treated with a concentrated solution of ammonium carbonate which slowly dissolves the beryllia. The filtered solution is boiled, and the well washed precipitate is dissolved in nitric acid, the solution evaporated to dryness, and the residue strongly heated. The beryllia thus obtained shows the spectra of no other metals.

C. H. B.

Purification of Beryllium Salts. By EDWARD HART (*J. Amer. Chem. Soc.*, 1895, **17**, 604—605).—The process depends on the fact that on adding sodium carbonate to an impure solution of beryllium sulphate, any iron and aluminium are precipitated first.

The powdered beryl is fused with potassium-sodium carbonate, ground and washed with water, mixed with sulphuric acid, and evaporated to render the silica insoluble. The bulk of the aluminium is then removed as alum by adding potassium sulphate, and, after oxidising any iron with potassium chlorate, it is, together with the remaining aluminium, precipitated by the cautious addition of sodium carbonate. After filtering, the beryllium is precipitated as carbonate.

L. DE K.

Beryllium Carbide. By PAUL LEBEAU (*Compt. rend.*, 1895, **121**, 496—499).—Pure beryllium oxide was intimately mixed with half its weight of sugar-carbon and a small quantity of oil, and heated in the electric tube furnace for eight to ten minutes with a current of 950 ampères and 40 volts. Less powerful currents yield a nitride or products containing nitrogen and carbon.

The beryllium carbide obtained under these conditions forms transparent, yellow-brown, microscopic crystals, similar to those of aluminium carbide, which it also resembles in chemical properties. The crystals scratch quartz easily; sp. gr. = 1.9 at 15°.

The carbide is readily attacked by chlorine at a dull red heat, with formation of beryllium chloride and a residue of amorphous carbon and graphite. Bromine behaves similarly at a somewhat higher temperature, but iodine has no action even at 800°. Oxygen produces superficial oxidation at a dull red heat, sulphur vapour attacks it below 1000°, but phosphorus and nitrogen have no appreciable action at dull redness. Dry hydrogen fluoride attacks the carbide with incandescence below a red heat, with formation of fluoride and liberation of carbon; hydrogen chloride behaves similarly, but with less energy. In contact with water or dilute acids, the carbide is slowly decomposed, with liberation of methane; the change occurring rapidly and completely in contact with a hot concentrated sodium or potassium hydroxide solution. It reduces concentrated boiling sulphuric acid, but is only slowly attacked by concentrated nitric or hydrochloric acids, although hot hydrofluoric acid dissolves it rapidly. Fused potassium hydroxide decomposes it with incandescence, potassium nitrate and chlorate are without action, but potassium permanganate and lead peroxide oxidise it readily.

The carbide has the composition Be_4C_3 ($\text{Be} = 13.8$), and no other carbide seems to exist.

C. H. B.

Beryllium Carbide. By LOUIS HENRY (*Compt. rend.*, 1895, **121**, 600—601).—It does not follow that because the beryllium carbide described by Lebeau (preceding abstract) is generally similar in its properties to aluminium carbide, it must be analogous in composition. Magnesia and silica are both in many respects similar to alumina. The analyses of the carbide quoted by Lebeau agree closely with the formula CBe_2 , and the apparent analogy between this compound and aluminium carbide cannot be allowed to over-ride the great weight of the other experimental evidence in fixing the valency of beryllium.

C. H. B.

Constitution of Metallic Bases. By NICOLAI KURNAKOFF (*J. pr. Chem.*, 1895, [2], 52, 490—528).—In continuation of his previous paper (*Abstr.*, 1895, i, 499), the author treats of the compounds in which ammonia replaces water of crystallisation, either wholly or in part, and reviews the theories which have been advanced in explanation of the existence of metallic ammonia salts of the general form $MX_m \cdot nNH_3$. These theories fall into three classes—(1) the ammonium theory, depending on the pentad nature of nitrogen; (2) the theory which regards the haloid or other acid radicle in the metallic salt as unsaturated; (3) the theory of higher types of metallic compounds as expounded by Mendeléeff. In connection with the last, the author quotes some results which he has obtained while investigating the refraction coefficient of solutions of the compounds $PtCl_2 \cdot 4NH_3$, K_2PtCl_6 , Na_2PtCl_6 , and $PtCl_2(NO_3)_2 \cdot 4NH_3$. None of the theories to which reference is made can, in the author's opinion, be regarded as furnishing the basis for a generalisation as to the constitution of the metallic bases, although each serves to throw light on the subject.

A. G. B

Mechanical Properties of Alloys of Copper and Zinc. By GEORGES CHARPY (*Compt. rend.*, 1895, 121, 494—496).—Alloys of copper and zinc, containing from 0 to 50 per cent. of the latter, were rolled and hammered in the cold until they were brought to a condition of maximum brittleness, and broke with practically no deformation. They were then annealed at various temperatures and subjected to tension and compression. For the crude cast alloys, the resistance depends on the temperature of casting and on the rate of cooling; it increases when the metal is cast near its melting point, and when the mould is arranged so as to produce rapid solidification.

The temperatures of annealing may be divided into four zones, which vary with the composition of the alloy. The first, or zone of *no annealing*, extends to about 350° for red copper, but the maximum limit falls as the proportion of zinc increases. The second, or zone of *variable annealing*, in which the degree of annealing varies continuously with the temperature, is almost unrecognisable for copper, but its range increases with the proportion of zinc, and for an alloy containing 40 per cent. of zinc it extends almost from the ordinary temperature up to the melting point. In the third, or zone of *constant annealing*, the effect on the mechanical properties is practically constant; the zone extends from about 400° to $1,000^\circ$ for copper, but diminishes as the proportion of zinc increases. In all three zones, annealing lowers the resistance and increases the extension before breaking.

The fourth zone comprises high temperatures near the melting points, and in these the metal undergoes deterioration or is "burnt," and both the resistance and the extension are reduced. The range of this zone seems to depend on the proportion of impurities present.

The resistance to tension increases with the proportion of zinc up to about 43 per cent., and then falls rapidly; the elongation before

breaking also increases with the proportion of zinc up to about 30 per cent., and then falls rapidly. The most useful alloys are those which contain from 30 to 43 per cent. of zinc; a high proportion of zinc corresponds to a higher resistance, and a high proportion of copper to a greater elongation before breaking.

C. H. B.

Oxidation of some Gases with Palladinised Copper Oxide.

By EDWARD D. CAMPBELL (*Amer. Chem. J.*, 1895, **17**, 681—692).—The palladinised copper oxide was prepared as follows:—(1) Copper was alloyed with palladium (1 per cent.), care being taken to cool the molten mass as quickly as possible; the alloy was then annealed, divided into small pieces, and oxidised in the tube. In the determinations given below, this oxide was employed. (2) Finely divided oxide, prepared by the preceding method, was mixed with gum, pressed into wire, and ignited. (3) Palladium (3 grams) was dissolved in aqua regia, and the solution, after removal of the excess of acid, mixed with finely divided copper oxide (300 grams); the stiff paste was dried at 120°, finely ground, mixed with gum, pressed into wire, and ignited. The temperatures given below are the initial combustion temperatures when the palladinised copper oxide is employed, those in brackets are the values obtained with pure copper oxide. Hydrogen 80—85° (175—180°), carbon monoxide 100—105° (100—105°), ethylene 240—250° (315—325°), propylene 220—230° (270—280°), isobutylene 270—280° (320—330°), methane no combustion at 455°. Acetylene, unlike the preceding gases, does not burn directly; at 395—400°, only $\frac{2}{3}$ of the carbon and $\frac{5}{8}$ of the hydrogen are oxidised, the remainder forms a black deposit in the tube. Full details are given of the apparatus employed, and the quantity of the various gases burnt per hour at different temperatures is also tabulated.

J. B. T.

Action of Hydrochloric acid on Copper. By RODOLPHE ENGEL (*Compt. rend.*, 1895, **121**, 528—530).—Hydrochloric acid saturated at 15° attacks copper somewhat rapidly with evolution of hydrogen, and the evolution of gas becomes tumultuous if the copper is previously immersed in a dilute solution of platinum chloride. No action takes place with a solution of a sp. gr. so low as 1.083, which corresponds with the composition $\text{HCl} + 10\text{H}_2\text{O}$. When the liquid is saturated with cuprous chloride, the action becomes very slow, even though the quantity of free acid present may considerably exceed the minimum limit just specified. Similar phenomena are observed with zinc and tin. A rise of temperature increases the action, and *vice versa*, doubtless in consequence of the variations in the solubility of the cuprous chloride. At the ordinary temperature, equilibrium is only established after a very long period.

When gaseous hydrogen chloride is passed into water containing copper and cuprous chloride, the acid is rapidly decomposed, notwithstanding the presence of the copper salt, and it follows that anhydrous hydrogen chloride is always decomposed by copper.

C. H. B.

Action of Nitric Oxide on certain Salts. By H. A. AUDEN and GILBERT J. FOWLER (*Chem. News*, 1895, **72**, 163).—The substances were exposed in a stream of nitric oxide at the ordinary temperature and at gradually increasing temperatures, and were weighed at intervals of temperature.

Lead dioxide, and also manganese dioxide, yields basic nitrate with but a trace of nitrite; with lead oxide, the action commences at 15° and reaches a maximum at 130°; with manganese oxide, the action is not so rapid, and is at its highest at 216°.

Moist silver oxide yields equivalent parts of nitrite and free metal at the ordinary temperature, whilst at higher temperatures the dry oxide yields silver and silver nitrate. Silver permanganate is attacked at the ordinary temperature, but at 80° the action is very sharp; the products being silver, silver oxide and nitrate, manganese dioxide, with little or no manganese nitrate. Potassium permanganate is not appreciably attacked below 100°, but vigorously at 190°, yielding potassium nitrate and manganese oxide.

Potassium chlorate, and also barium chlorate, yield chlorine and nitrogen peroxide at the ordinary temperature; the percentage of chlorine in the gaseous product being below that required to form nitrosyl or nitroxyl chloride; the solid product is the nitrate, with a trace of perchlorate, but no chloride. Silver chlorate also yields chlorine in abundance, but at the same time a large proportion of silver chloride is formed. Potassium iodate commences to evolve iodine at 80°, and at 110° the evolution is rapid; nitrate without iodide remains. Silver iodate, on the other hand, at about 110°, yields silver iodide without any evolution of iodine. Potassium perchlorate at above 200° yields abundance of chlorine, leaving a residue of nitrate with a small quantity of chloride; this is attributed to secondary reactions resulting from the high temperature. Barium periodate behaves in a similar manner.

Lead chromate is not attacked at above 400°, but above 300° silver chromate yields silver, silver nitrate and nitrite, and chromic oxide. Silver sulphate is slightly attacked at the highest temperature.

Mixing lead or manganese dioxide with lead nitrate caused the action to take place at a lower temperature than when either the oxide or salt was separately exposed to nitric oxide. D. A. L.

Tempering of very hard Steel. By FLORIS OSMOND (*Compt. rend.*, 1895, **121**, 684—686).—If a bar of cementation steel in which the proportion of carbon varies continuously from, say, 0.35 per cent. at one end to 1.70 per cent. at the other, is given a very high temper, it is found that it can be scratched by a needle up to 0.70 per cent. of carbon, cannot be scratched with a higher proportion up to 1.3 per cent., but beyond this point can again be scratched. Microscopic examination shows, however, that the more carbonaceous part is not homogeneous, but contains two constituents: A, which is scratched by glass and orthoclase, although not by a needle; and B, which is scratched by apatite and perhaps by fluorspar. On a well-polished surface, B is silver-white, whilst A is greyish. The action of iodine solution or of dilute nitric acid shows that the mass consists of poly-

hedra, sometimes separated, sometimes not, by the carbide Fe_3C . Generally, A is distributed in pointed lamellæ parallel with two directions which remain constant for each polyhedron, whilst B forms the matrix. Both A and B contain carbon. The constituent A is identical with that which is almost the only constituent of tempered steel containing 1 per cent. of carbon. The proportion of B increases with the proportion of carbon up to about 1.6 per cent., and beyond this point the carbide Fe_3C (?) separates in increasing quantities.

In order to obtain the maximum proportion of B, the steel must be heated to at least 1000° , although nothing is gained by going beyond 1100° , and cooled as rapidly as possible, either in ice-cold water or in very cold mercury, otherwise the carbide Fe_3C separates. Under favourable conditions, the metal will be a mixture of A and B, in approximately equal quantities. Such a mixture is comparatively feebly magnetic, whilst a bar of the same metal heated at 800° and cooled in water at 15° is strongly magnetic, and retains permanently a higher proportion of the magnetisation imparted to it. It would seem that B is not magnetic. The metal containing equal parts of A and B cannot be filed, and breaks without bending, as much by reason of the presence of the hard and brittle constituent A as because of the want of cohesion between the polyhedra. It is, however, slightly malleable.

The properties of B seem to be similar to those of highly nickeliferous and manganiferous steels, which contain iron in the allotropic form γ , stable above 860° .

C. H. B.

Reduction of Iron Oxides by Carbonic Oxide. By ISAAC BRAITHWAITE (*Chem. News*, 1895, **72**, 211).—At a low red heat, carbonic oxide is found to be oxidised more readily by ferric oxide than by triferric tetroxide, whilst ferrous oxide is still less active. Conversely, carbonic anhydride is reduced more quickly by iron than by ferrous oxide, and not at all by triferric tetroxide.

D. A. L.

Action of Silicon on Iron, Chromium, and Silver. By HENRI MOISSAN (*Compt. rend.*, 1895, **121**, 621–626).—*Iron silicide*, SiFe_2 , is obtained (1) by heating iron to the softening point of porcelain in a porcelain dish brasqued with silicon. (2) By heating iron with one-tenth its weight of silicon in a crucible in the electric furnace for four minutes with an arc from a current of 900 ampères and 50 volts. With a higher proportion of silicon, the product is not attacked by acids. (3) By heating in the electric furnace a mixture of ferric oxide with excess of silicon, silica being volatilised.

In all cases, the product is treated with nitric acid diluted with four times its volume of water.

The iron silicide forms small, magnetic, prismatic crystals, with a metallic lustre; sp. gr. = 7.00 at 22° . Its melting point is higher than that of cast iron and lower than that of wrought iron. Hydrofluoric acid attacks it readily, and hence it is not identical with the silicide which Hahn described as not attacked by this acid. Hydrochloric acid slowly attacks the finely powdered silicide; nitric acid

has no action, but aqua regia decomposes it, with formation of silica. The gaseous hydracids attack it at temperatures varying from dull to bright redness. Potassium nitrate and chlorate, at their melting points, have no action on it; fused alkali carbonates attack it slowly, and a fused mixture of a nitrate and a carbonate decomposes it readily.

When cylinders of soft iron are embedded in crystals of silicon and heated at the temperature of a good forge, the silicon penetrates to the centre of the cylinders, although the iron does not fuse, and a silicide is formed. This result is a further proof that silicon has a distinct vapour tension below its melting point.

Chromium silicide, SiCr_2 , is obtained (1) by heating chromium in a dish lined with silicon at a temperature somewhat above 1200° in a current of hydrogen. (2) By heating pure chromium with 15 per cent. of its weight of silicon in a carbon crucible in an electric furnace for nine minutes with an arc from a current of 900 ampères and 50 volts. (3) By heating in the electric furnace for ten minutes with an arc from a current of 950 ampères and 70 volts, a mixture of 60 parts of silica, 200 parts of chromic oxide, and 70 parts of sugar-carbon. The product is treated with cold concentrated hydrofluoric acid, the temperature being kept down, if necessary, by the addition of water. The silicide forms small, prismatic crystals, very similar in properties to the iron silicide, but less easily attacked by hydrofluoric acid, and more easily by fused potassium nitrate. It scratches quartz, and even corundum, quite easily.

Silver, when heated with silicon in the electric furnace, dissolves a considerable quantity, but the silicon separates as the metal cools, and no silver silicide is obtained, nor does the silver retain any silicon. Some crystals of carbon silicide are often formed.

It follows that (1) solid silicon may unite with a solid metal by reason of its vapour tension, in a manner analogous to cementation; (2) liquid silicon unites with a liquid metal; and (3) silicon may dissolve in a liquid metal, forming either a very unstable compound or no compound at all, and being liberated in a crystalline state as the metal solidifies.

C. H. B.

Some Alloys of Iron with Molybdenum, Tungsten, and Chromium. By JAMES S. DE BENNEVILLE (*J. Amer. Chem. Soc.*, 1894, 16, 735—757).—The alloys of iron with the metals of the tungsten group have been examined; they were prepared by melting down cast iron with the metals at a white heat in a small Fletcher's furnace working with a blast, this temperature being maintained for one hour. Whereas unalloyed molybdenum is practically infusible in furnaces worked with a blast, its iron alloys fuse at a much lower temperature. Molybdenum alloys, containing 16.6 and 29.8 per cent. of the metal, were prepared, and tungsten alloys containing 46.5 and 17 per cent. of tungsten, whilst with chromium, only a single alloy, containing 7 per cent. of that metal, was prepared. The physical properties of these alloys were noted, but the especial object of the investigation was the action of the weak solvent, silver nitrate, on the alloys, together with their behaviour with liquid and fused solvents. The

more important conclusions drawn from the results thus obtained are : That these alloys, by their resistance to chemical reagents, their hardness and increased specific gravity, indicate a chemical union between the constituents. That in these alloys a number of compounds are present, some of which are more stable than others, the latter class being readily attacked by weak solvents. That these compounds are distributed with considerable uniformity throughout the mass of the alloy, segregation being the exception, not the rule, and that their freezing points must be approximately the same, preventing the segregation of alloys of great density in any one portion of the alloy ; that the more stable of these alloys are definite chemical compounds ; that the less stable may be definite compounds, or of the nature of cryohydrates, or with one of the constituents present in the mixture in a state analogous to that of ice in a frozen salt solution, in which water is in excess.

J. J. S.

Two Definite Carbides of Iron with Chromium (Molybdenum and Tungsten). By JAMES S. DE BENNEVILLE (*J. Amer. Chem. Soc.*, 1895, **17**, 791—801).—In the course of his work on ternary alloys of iron with chromium, molybdenum, and tungsten, the author prepared two definite carbides. These were obtained from chromium alloys, and only from those two in which chromium was the predominant metal. They formed well defined crystals, differing in form and reactions from the matrix in which they were embedded. The separation of the crystals was effected by the action of nitric acid, which left them intermixed with a little silica. This was removed as silicon fluoride, and, after washing with water and subsequently with alcohol, the crystals were obtained free from impurity. They are remarkably inert, not being acted on by hydrochloric, nitric, or hydrofluoric acid. Concentrated sulphuric acid slowly decomposes them, leaving a black residue ; they are readily decomposed at a red heat by chlorine, bromine, or iodine, but their analysis is best effected by fusing with a mixture of sodium carbonate and hydroxide, and potassium nitrate. The results obtained were

	Fe.	Cr.	Mo.	W.	C.	Total.
I.	46.39	46.23	2.01	—	5.53	100.16
II.	47.24	35.42	—	11.39	5.95	100.00

J. J. S.

The Ferrates. By CLAUDE A. O. ROSELL (*J. Amer. Chem. Soc.*, 1895, **17**, 760—769).—This paper opens with a short history of the ferrates, mentioning the work of Stahl, Ekeberg, Becquerel, Fremy, Denham Smith, Rose, and Bloxam.

The author has attempted to prepare sodium ferrate in the dry way, according to Stahl's method, by calcining ferric oxide with sodium hydroxide, carbonate and nitrate, and with mixtures of sodium hydroxide and nitrate, and also with sodium nitrate and carbonate, but in vain. Sodium peroxide was also tried, and, when the resulting mixture was treated with ice instead of water, a solution of sodium ferrate was obtained. Attempts to obtain iron dioxide by

the action of an alkaline ferric solution on the solution of the ferrate, or by the addition of barium ferrate to a solution of ferric chloride, proved useless.

The most stable ferrate is the barium compound, $\text{BaFeO}_4 + \text{H}_2\text{O}$; whereas calcium ferrate is readily soluble in water, the barium compound is insoluble; before drying, it is readily decomposed by all acids, even carbonic, but after drying it is not so readily acted on. An alkali sulphate decomposes barium ferrate, if it has not been dried, with the formation of barium sulphate and ferric hydroxide, oxygen being set free. It is further shown, that the emerald green solution obtained by Fremy on passing hydrogen sulphide through a solution of sodium ferrate, is due to the presence of manganese. The question as to whether ferrates more closely resemble chromates or manganates is discussed. So far as their oxidising properties are concerned, they resemble the manganates; a ferrate will readily oxidise nitrites, tartrates, and glycerol; the soluble ferrates are also reduced by oxalates, alcohol, urea, ether, ammonia, &c., and by most soluble organic compounds, with the exception of the acetates. The simplest method for preparing solutions of sodium or potassium ferrate is to pass chlorine into a solution of the corresponding hydroxide, containing ferric hydroxide in suspension. J. J. S.

Nickel and Cobalt Silicides. By VIGOUROUX (*Compt. rend.*, 1895, 121, 686—688).—When nickel or cobalt is heated with 10 per cent. of silicon in a current of hydrogen, in a reverberatory furnace, combination takes place, with formation of a crystalline product more fusible than the metal. Similar results are obtained by heating the silicon and the metal in a Doulton crucible in an oxyhydrogen furnace. Heating silicon with the oxides of the metals in either form of furnace does not yield a pure product. The best results are obtained by heating the metals with 10 per cent. of silicon, in carbon crucibles in the electric furnace, until the greater part of the excess of the metal is volatilised. The product is treated with very dilute nitric acid.

The silicides, SiNi_2 or SiCo_2 , are perfectly crystallised, and have a metallic appearance, and a steel-grey colour; they are more fusible than the metal or silicon, and are stable at the highest temperatures. The sp. gr. of the nickel silicide is 7.2 at 17° , and that of the cobalt silicide 7.1. Fluorine attacks them with incandescence at the ordinary temperature, and chlorine has the same effect at a red heat; bromine and iodine are less energetic in their action. Dry hydrogen fluoride and hydrogen chloride attack them at a red heat, and hydrogen bromide and iodide behave similarly. Hydrofluoric acid dissolves them readily, but the other haloid acids act very slowly; aqua regia, however, decomposes the powdered substances completely. Water has no action on the crystals, but water vapour attacks them at a dull red heat. Oxygen or air oxidises the finely powdered silicides at a red heat. Solutions of alkali hydroxides are without effect, but fused alkali carbonates or mixtures of carbonates and nitrates decompose them readily. C. H. B.

New Solvents of Perchromic acid. By WILLIAM M. GROSVENOR, Jun. (*J. Amer. Chem. Soc.*, 1895, **17**, 41—43).—The author finds that ethylic acetate and valerate, amylic valerate, amylic chloride, amylic butyrate, formate, and acetate all dissolve perchromic acid, yielding blue solutions similar to that given by ether. Carbon bisulphide, benzene, light petroleum, turpentine, castor oil, wintergreen oil, bergamot oil, paraffin, chloroform, carbon tetrachloride, toluene, nitrobenzene, and aniline do not dissolve it.

The solution in ethylic acetate is the most stable, but even that turns colourless after 23 hours. The author does not agree with Griggi (*Abstr.*, 1893, ii, 233) in stating that the solution in amylic alcohol is more stable than that in ordinary ether. J. J. S.

Uranium Oxynitride and Uranium Dioxide. By EDGAR F. SMITH and J. MERRITT MATTHEWS (*J. Amer. Chem. Soc.*, 1895, **17**, 686—688).—To prepare the oxynitride, uranyl chloride was placed in a porcelain boat and heated in a current of dry ammonia, when, at a comparatively low temperature, the material assumed a dark colour, and copious fumes of ammonium chloride were evolved; the heat was then raised and continued until no more fumes were given off, and a dull black residue free from chlorine was left. This, when fused in a nickel crucible with potassium hydroxide, slowly evolved ammonia. When introduced into solution of silver nitrate, brilliant crystals of metallic silver were formed. When heated in a sealed tube with dilute sulphuric acid (1—2), complete solution ensued, and titration with potassium permanganate showed that 6·83 per cent. of dioxide was present. An estimation of the uranium and the nitrogen gave figures closely corresponding with the formula $U_{11}N_6O_{25}$.

In order to obtain the dioxide, the authors heated the oxide, U_3O_8 , with a large excess of ammonium chloride in a porcelain crucible, which was placed in a larger Hessian one, and the whole surrounded with charcoal closely packed; the crucibles were heated in a wind furnace at a white heat for about six hours. The reddish-brown residue was free from chlorine and nitrogen; the percentage of uranium was found to be 88·12 per cent. When heated over a Bunsen flame, it changed gradually, but completely, into uranouranic oxide. L. DE K.

Alloys of Copper and Tin. By FRITZ FOERSTER (*Zeit. anorg. Chem.*, 1895, **10**, 309—319).—The author has prepared alloys of copper and tin containing from 1 to 28 per cent. of copper. These alloys, when broken in coarse pieces and treated with cold, fuming, hydrochloric acid, yield, a grey, lustrous, crystalline residue consisting of hard, brittle lamellæ. In the case of the alloy containing only 1 per cent. of copper, minute, lustrous needles were also obtained. These crystalline residues are only slightly attacked by ammonia, and very slowly oxidised by dilute nitric acid. They precipitate copper from neutral solutions of its salts, although much more slowly than pure tin, but do not precipitate copper from a solution of cuprous chloride in hydrochloric acid. The composition of the residues varies

from 38.52 per cent. Cu and 61.42 per cent. Sn to 55.95 per cent. Cu and 43.67 per cent. Sn. The residue, containing 55.95 per cent. of copper, when treated with strong hydrochloric acid for 2—3 days, yielded a residue containing 61.47 per cent. Cu and 38.88 per cent. Sn. These residues probably contain mixtures of two compounds of the composition Cu_3Sn and CuSn . The residues obtained from the alloys poorest in copper have the same composition as those obtained from those portions of an alloy richer in copper which remain fluid longest, that is, the crystals first deposited are richer in copper than those obtained at a lower temperature from the mother liquor. The residues richest in tin begin to decompose when heated above 300° , whereby drops of tin or of a dilute solution of copper in tin are separated: this can be dissolved out by treating the mixture with hydrochloric acid, and the residue thus obtained approaches the compound Cu_3Sn in composition (see also Le Chatelier, *Abstr.*, 1895, ii, 351).

E. C. R.

Action of Hydrogen Peroxide on Fluorides and Oxyfluorides. By AUGUSTO PICCINI (*Zeit. anorg. Chem.*, 1895, **10**, 438—445).—Potassium fluoroxypertitanate, $\text{TiO}_2\text{F}_2 \cdot 2\text{KF}$, is obtained mixed with the fluorotitanate when a hot solution of potassium fluorotitanate, $\text{TiF}_4 \cdot 2\text{KF} \cdot \text{H}_2\text{O}$, is treated with hydrogen peroxide. When this precipitate is dissolved in hydrogen peroxide and the mixture neutralised with sodium peroxide, a crystallisation richer in fluoroxypertitanate is obtained, but the salt cannot be obtained pure. A fairly pure product is obtained as a yellow, crystalline powder, when a cold solution of triammonium fluoroxypertitanate, $\text{TiO}_2\text{F}_2 \cdot 3\text{NH}_4\text{F}$, is precipitated with potassium chloride.

Ammonium fluoroxypertitanates, $m\text{TiO}_2\text{F}_2 \cdot n\text{NH}_4\text{F}$. When a solution of ammonium fluorotitanate is treated with hydrogen peroxide in the presence of ammonia and ammonium fluoride, the salt, $\text{TiO}_2\text{F}_2 \cdot 3\text{NH}_4\text{F}$, is obtained as a yellow precipitate. It crystallises from water in small, yellow octahedra. It is also obtained by treating a solution of titanic acid in sulphuric acid with barium peroxide, then with ammonia until a permanent precipitate is formed, and finally precipitating with neutral ammonium fluoride. It is also obtained by allowing ammonium fluorotitanite, $\text{TiF}_3 \cdot 3\text{NH}_4\text{F}$, washed with a concentrated solution of ammonium fluoride, and moistened with alcohol to oxidise in the air. A small quantity of the salt, $2\text{TiO}_2\text{F}_2 \cdot 3\text{NH}_4\text{F}$, crystallising in yellow needles, is also obtained. If the solution of the salt obtained by the last method is mixed with ammonium fluoride, a crystalline precipitate of the salt $\text{TiO}_2\text{F}_2 \cdot 3\text{NH}_4\text{F}$, is obtained.

From the results here obtained and the author's previous work (*Zeit. anorg. Chem.*, **1**, 51, and **2**, 21), the action of hydrogen peroxide on the oxyfluorides of molybdenum, tungsten, and niobium, and on the fluorides of tantalum and titanium can be expressed by the following equations. $\text{MoO}_2\text{F}_2 + \text{H}_2\text{O}_2 = \text{MoO}_3\text{F}_2 + \text{H}_2\text{O}$. $\text{WO}_2\text{F}_2 + \text{H}_2\text{O}_2 = \text{WO}_3\text{F}_2 + \text{H}_2\text{O}$. $\text{NbOF}_3 + \text{H}_2\text{O}_2 = \text{NbO}_2\text{F}_3 + \text{H}_2\text{O}$. $\text{TaF}_5 + \text{H}_2\text{O}_2 = \text{TaO}_2\text{F}_3 + 2\text{HfF}$. $\text{TiF}_4 + \text{H}_2\text{O}_2 = \text{TiO}_2\text{F}_2 + 2\text{HfF}$. The fluoroxyanhydrides of the type of hydrogen peroxide

react with metallic fluorides, whereby compounds are formed corresponding with those obtained from the fluoroxyanhydrides and the fluoranhydrides of the type of water. The fluoroxy-salts of the type of hydrogen peroxide are analogous in composition and crystalline form to those of the type of water. They can be obtained in analogous ways, but differ from the latter in colour, in the ease with which they give up part of their oxygen and in the property they possess of reducing potassium permanganate in acid solution.

E. C. R.

Double Fluorides of Cæsium and Zirconium. By HORACE L. WELLS and H. W. FOOTE (*Zeit. anorg. Chem.*, 1895, **10**, 434—437).—The double salts are prepared by mixing the solutions of the fluorides in various proportions in the presence of more or less hydrofluoric acid, and then evaporating the mixture to crystallisation.

The salt, $2\text{CsF} \cdot \text{ZrF}_4$, is obtained by employing an excess of cæsium fluoride. It crystallises in large, hexagonal tablets, and can be recrystallised without decomposition.

The salt, $\text{CsF} \cdot \text{ZrF}_4 + \text{H}_2\text{O}$, is obtained in the presence of larger quantities of zirconium fluoride. It separates in monoclinic crystals, and can be recrystallised without decomposition.

The salt, $2\text{CsF} \cdot 3\text{ZrF}_4 + 2\text{H}_2\text{O}$, is obtained in the presence of a large excess of zirconium fluoride. It separates from the solution in small, sparingly soluble crystals, and when recrystallised is partially converted into the 1 : 1-salt.

E. C. R.

Action of Phosphorus Pentachloride on Zirconium and Thorium Dioxides. By EDGAR F. SMITH and HARRY B. HARRIS (*J. Amer. Chem. Soc.*, 1895, **17**, 654—656).—The work was undertaken to complete the investigation commenced by Weber.

The dioxides of zirconium and thorium were introduced into hard glass tubes together with the equivalent of phosphorus pentachloride; the tubes being then exhausted and sealed. After heating for eight hours at 190° , a complete change was observed, a crystalline mass and drops of phosphorus oxychloride being scattered through the tube. After opening the tube at both ends, the contents were heated in a current of chlorine, part of the tube being heated in an air bath at 190° , when large, transparent crystals collected in the projecting cold part of the tube. Analysis proved them to consist of the corresponding chlorides.

L. DE K.

Iridio-ammonium Compounds. By WILHELM PALMAER (*Zeit. anorg. Chem.*, 1895, **10**, 320—386; see also Abstr., 1889, 352, and 1891, 402 and 1165).—When iridium chloride is treated with ammonia in an ordinary reflux apparatus, about 48 per cent. of a double salt of the composition $\text{Ir}(\text{NH}_3)_3\text{Cl}_3$ is obtained, together with the pentamine chlorochloride, a tetramine compound, $\text{Ir}(\text{NH}_3)_4\text{Cl}_3 \cdot \text{H}_2\text{O}$, and the aquopentamine chloride, $\text{Ir}(\text{NH}_3)_5\text{OH}_2\text{Cl}_3$. When 50 c.c. of a solution of iridium trichloride, containing 5 grams of metal mixed with 150 c.c. of 25 per cent. ammonia, is heated in a Liutner's

pressure flask at 100° for 10 hours, the following products are obtained. Iridium hydroxide corresponding with 0.11 gram of metal. This is separated by filtration, and the filtrate evaporated on the water bath to dryness, whereby all the aquopentamine chloride is converted into pentamine chlorochloride. The dry residue is treated with cold water, whereby ammonium chloride and the tetramine chloride are dissolved. The residue insoluble in cold water is dried on the water bath and treated with cold concentrated sulphuric acid, whereby chlorosulphate is formed, and any double salt (about 1 gram) which is present remains undissolved. The sulphuric acid solution is finally treated with fuming hydrochloric acid, and the pentamine chloride filtered off. 7.4 grams are obtained.

Iridiopentamine chlorochloride, $\text{Ir}(\text{NH}_3)_5\text{ClCl}_2$, has already been described (Abstr., 1891, 402). The red coloration of the salt prepared as above is due to a very minute trace of iridium trichloride, which can be separated by treating the hot aqueous solution with hydrogen sulphide. It crystallises in yellowish-white octahedra; when heated at high temperatures, it yields metal, ammonium chloride, and ammonia; it is completely precipitated from its aqueous solution by hydrochloric acid.

The *chlorhydroxide*, $\text{Ir}(\text{NH}_3)_5\text{Cl}(\text{OH})_2$, is obtained by treating the chlorochloride with freshly prepared silver oxide. It is very stable, absorbs carbonic anhydride from the air, and is slowly decomposed when boiled with water. It is also obtained by warming the chlorochloride with sodium hydroxide on the water bath. The *acid chlorosulphate*, $4\text{Ir}(\text{NH}_3)_5\text{ClSO}_4 + 3\text{H}_2\text{SO}_4 + 3\text{H}_2\text{O}$, is obtained by dissolving the chlorochloride (1 gram) in concentrated sulphuric acid (2 c.c.) and then adding water (10 c.c.). It crystallises in lustrous, bright yellow prisms, is easily soluble in water, and has an acid reaction. The *chlorodithionate*, $\text{Ir}(\text{NH}_3)_5\text{ClS}_2\text{O}_6$, is obtained by adding barium dithionate to a cold saturated solution of the chlorochloride. It crystallises in long, six-sided prisms, and with $1\text{H}_2\text{O}$ in thick, four-sided prisms. The *chloroxalate*, $\text{Ir}(\text{NH}_3)_5\text{ClC}_2\text{O}_4$, crystallises in slender, white needles.

Iridiopentamine chlorochloriridite, $3\text{Ir}(\text{NH}_3)_5\text{ClCl}_2 + 2\text{IrCl}_3$, is obtained by mixing the solution of the chlorochloride with one of the trichloride as a flocculent precipitate, and from the remaining solution as a crystalline, yellow powder on evaporating it on the water bath. It is only slowly attacked by sulphuric acid at 110° , and is decomposed by heat, yielding iridium, ammonium chloride, and hydrogen chloride. The pentamine chloro-salts here mentioned, together with those previously described, are neutral, with the exception of the acid sulphate and the nitrite which has an alkaline reaction.

Iridiopentamine bromobromide, $\text{Ir}(\text{NH}_3)_5\text{BrBr}_2$, has been previously described. It is best obtained by boiling the pentamine chlorochloride with potassium hydroxide for about five hours, when the aquopentamine hydrate is formed. The solution is saturated with 50 per cent. hydrobromic acid, whereby a white, crystalline precipitate of the aquopentamine bromide, $\text{Ir}(\text{NH}_3)_5\text{OH}_2\text{Br}_3$, is obtained, and, by heating the solution of the latter salt on the water bath, it is

converted into the bromobromide. This crystallises in yellow, rhombic prisms, $a : b : c = 0.9752 : 1 : 1.5687$, is soluble in 352 parts of water at 12.5° , and has a sp. gr. of 3.245 at 16.5° . The bromonitrite crystallises in yellow, rhombic prisms, $a : b : c = 0.969 : 1 : 1.535$, and is isomorphous with the pentamine chloronitrite.

Iridiopentamine iodoiodide, $\text{Ir}(\text{NH}_3)_5\text{I}_2$, is obtained by heating the aquopentamine hydrate at 100° . It crystallises in thick six-sided prisms and octahedra, belonging to the rhombic system $a : b : c = 0.993 : 1 : 1.552$, is soluble in 770 parts of water at 14° , and 50 parts of boiling water, and has the sp. gr. of 3.586 at 15.5° .

Iridiopentamine nitratonitrate, $\text{Ir}(\text{NH}_3)_5\text{NO}_3(\text{NO}_3)_2$, is obtained by heating the aquopentamine nitrate at 100° . It crystallises in microscopic, quadratic tablets, explodes when heated, dissolves in 349 parts of water at 16° and in 40 parts of boiling water, and has the sp. gr. of 2.510 at 18.5° .

Iridioaquopentamine chloride, $\text{Ir}(\text{NH}_3)_5\text{OH}_2\text{Cl}_3$, the aquopentamine bromide and the aquopentamine nitrate have already been described.

Iridioaquopentamine iodide, prepared in a similar way to the above aquopentamine salts, is a white, crystalline powder, having a yellowish-brown fluorescence; it is converted into the pentamine iodide when heated, dissolves in 15 parts of water, and has the sp. gr. of 3.253 at 14° . The *aquopentamine chloriridite*, $\text{Ir}(\text{NH}_3)_5\text{OH}_2\text{Cl}_3\cdot\text{IrCl}_3$, is obtained by adding iridium trichloride to a solution of the aquopentamine chloride in dilute hydrochloric acid. It is a yellowish-brown, crystalline precipitate, insoluble in water, and is not attacked by cold, concentrated sulphuric acid.

Iridiohexamine chloride, $\text{Ir}(\text{NH}_3)_6\text{Cl}_3$, is obtained by heating the pentamine chlorochloride (2 grams) with 25 per cent. ammonia (20 c.c.) in a sealed tube at 140° for 48 hours. The product is evaporated to dryness with hydrochloric acid, dissolved in water, and the filtered solution precipitated with sodium pyrophosphate. The washed precipitate of iridiohexamine sodium pyrophosphate is dissolved in dilute hydrochloric acid and precipitated with nitric acid, whereby the hexamine nitrate is obtained. The nitrate is then evaporated to dryness two or three times with hydrochloric acid, and the solution of the product cooled with ice and precipitated with ice-cold, fuming hydrochloric acid. It crystallises in large, colourless, six-sided prisms belonging to the monosymmetric system $a : b : c = 0.5843 : 1 : 0.6502$; $\beta = 57^\circ 31'$, and gives measurements very closely agreeing with those of Klein's luteocobalt chloride (*Annalen*, **166**, 188). It is soluble in 4.5 to 5 parts of water, and has the sp. gr. of 2.4335 at 15.5° . The *hexamine hydroxide*, $\text{Ir}(\text{NH}_3)_6(\text{OH})_3$, is obtained in solution by treating the preceding salt with silver oxide. The solution is strongly alkaline, displaces ammonia from ammonium salts, and gives precipitates of the metallic hydroxides with solutions of aluminium and zinc salts. On exposure to air, it is converted into the carbonate which crystallises in crusts of microscopic six-sided tablets. The *hexamine bromide*, $\text{Ir}(\text{NH}_3)_6\text{Br}_3$, obtained by precipitating a solution of the nitrate with hydrobromic acid, crystallises in colourless six-sided prisms similar to those of the hexamine chloride; it is soluble in 28—30 parts of water, and has the sp. gr. of 2.942 at

15.5°. The *hexamine iodide*, $\text{Ir}(\text{NH}_3)_6\text{I}_2$, is obtained by treating the hexamine hydroxide with excess of hydriodic acid. It crystallises in yellowish, lustrous tablets and pyramids, gives off iodine vapours when heated, is soluble in 91 parts of water at 18°, and has the sp. gr. of 3.291 at 16.5°. The *hexamine nitrate*, $\text{Ir}(\text{NH}_3)_6(\text{NO}_3)_3$, crystallises in large, quadratic tablets belonging to the tetragonal system $a:b = 1:1.042$, and isomorphous with the luteocobalt nitrate; it is soluble in 59 parts of water at 14°, and has the sp. gr. of 2.395 at 15°. *Iridiohexamine ferricyanide*, $\text{Ir}(\text{NH}_3)_6\text{Fe}(\text{CN})_6$, is obtained by adding potassium ferricyanide to a solution of the hexamine chloride in hydrochloric acid. It crystallises in orange-red prisms, and is very sparingly soluble in water. *Iridiohexamine chloriridite*, $\text{Ir}(\text{NH}_3)_6\text{Cl}_3\text{IrCl}_3$, is obtained as an amorphous, yellowish precipitate which is greyish-yellow when dry. From dilute solutions, it separates in small, quadratic tablets. It is insoluble in cold water, is attacked by concentrated sulphuric acid at 190°, and, when boiled with it, yields a clear, bright yellow solution. The solutions of the hexamine salts are neutral.

The reactions of the various classes of salts are described in detail in the original paper.

E. C. R.

Mineralogical Chemistry.

Native Sulphur in Michigan. By W. H. SHERZER (*Amer. J. Sci.*, 1895, [3], 50, 246—248).—In a band of carbonaceous limestone in the Upper Helderberg Limestone of Monroe Co., are cavities containing calcite, celestite, sulphur, and rarely selenite. In the same quarry is a stream of water highly charged with hydrogen sulphide, from which sulphur is now being deposited. It is suggested that the hydrogen sulphide has been derived from pyrites, marcasite, &c., or, perhaps, from the organic matter in the neighbouring rocks.

L. J. S.

Black Carbonado from Brazil. By HENRI MOISSAN (*Compt. rend.*, 1895, 121, 449—450).—A specimen of carbonado found in the province of Bahia, Brazil, weighed 630 grams (or 3073 carats), and is the largest that has yet been found. It is rounded in form, has a full black colour, and resembles in the character of its surface, &c., the microscopic grains of carbon obtained from ingots of silver or iron compressed by sudden external cooling. It is somewhat porous, and originally weighed 3167 carats, but lost about 19 grams during exposure to air for two months.

C. H. B.

Graphite from a Pegmatite. By HENRI MOISSAN (*Compt. rend.*, 1895, 121, 538—541).—An American pegmatite, containing 12·77 per cent. of graphite, was decomposed by means of hydrofluoric acid. The graphite was thus obtained in flexible, lustrous lamellæ, the surfaces of which showed striæ in the form of equilateral triangles; it began to burn in oxygen at 690°, and left 5·01 per cent. of ash, which consisted mainly of silica, alumina, and calcium oxide, with only a

trace of iron. The graphite was intumescent like that obtained by dissolving carbon in metals. Moreover, when treated with nitric acid and potassium chlorate, it increases enormously in volume.

Microscopic examination of the pegmatite proved that the faces of the crystals of quartz or felspar in contact with the lamellæ of graphite showed triangular striæ precisely similar to the striæ on the lamellæ. It follows that the graphite must have been pre-existent in the material from which the pegmatite was formed, and when the latter solidified, the graphite was compressed between the crystals of quartz or felspar.

C. H. B.

Gallium and Indium in a Blende from Peelwood, N.S.W.

By J. BOOTH KIRKLAND (*Australian Assoc. Adv. Sci., Fourth Report*, [1892] 1893, 266—267).—A peculiar, grey zinc ore from the above locality showed by the spectroscope the lines of gallium and indium. Crude chlorides of these metals have been extracted. Analysis of the ore gave

SiO ₂ .	Pb.	Fe.	Cu.	Zn.	S.	Total.
6.05	16.71	11.06	5.00	29.77	29.21	97.70

L. J. S.

The Senarmontite of Nieddoris, and the Minerals which accompany it, Arite, Breithauptite, Gersdorffite, and Smaltite. By DOMENICO LOVISATO (*Jahrb. f. Min.*, 1895, ii, Ref., 230—231; from *Atti R. Acc. Lincei, Rend.*, 1894, 3, 82—89).—The nickel ores of Nieddoris, in the mining district of Arbus, Sardinia, consist of a mixture of several minerals. Of these a light red mineral gave analysis I; this agrees with arite, and has the formula $9\text{RAs} + 5\text{RSb}$. A dark red ore gave II, this agreeing with the formula $\text{RAs} + 4\text{RSb}$, and is thus a mixture consisting principally of breithauptite. A dark, black mineral gave III, agreeing with the formula $(\text{Ni,Fe,Co})_2(\text{S,As,Sb})_3$, which comes near to gersdorffite, with, perhaps, some admixed ullmannite. The silver-white portion of the ores gave IV (with 2.14 per cent. of gangue), agreeing with the formula $(\text{Ni,Fe,Co})\text{As}_2$, and corresponding with smaltite (or chloanthite).

	S.	As.	Sb.	Ni.	Co.	Bi.	Fe.	Zn.	Pb.	Total.
I.	0.85	29.82	26.57	36.81	3.91	0.99	0.98	trace	—	99.93
II.	1.00	8.42	23.63	60.07	3.65	1.55	1.81	—	—	100.13
III.	13.72	44.78	3.11	35.12		0.91	2.36	—	—	100.00
IV.	2.94	58.76	1.06	9.85	7.65	—	9.86	0.72	6.33	97.17

IV contained in addition 2.14 of gangue.

Senarmontite and valentinite occur with these ores.

L. J. S.

Hercynite from Valtellina. By GOTTLÖB ED. LINCK (*Ber. Akad. Berlin*, 1893, 47—53).—In an altered gabbro, from near the Italian-Swiss frontier, are large, black, fine-grained masses, containing black grains of a spinel, sometimes showing octahedral faces, together with plagioclase, biotite, sillimanite, corundum, rutile, and a yellowish metallic ore. In sections, the spinel is green and transparent, and often encloses what appears from the analyses to be pyrrhotite. On

crushing the mass some hydrogen sulphide is given off. Analysis of the magnetic spinel and pyrrhotite gave I; II is the same neglecting impurities; sp. gr. of the pure material, 4.0108.

Al_2O_3 .	Fe_2O_3 .	FeO .	MgO .	SiO_2 .	Fe .	S .	Total.
59.62	3.10	25.30	9.38	1.59	1.79	1.02	101.80
61.21	3.18	25.98	9.63	—	—	—	100.00

This gives $\text{R}_2\text{O}_3:\text{RO} = 6200:6016$, the FeO being too low. Hercynite can only be distinguished from other green spinels by analysis. L. J. S.

Northupite, a new Mineral. By WARREN M. FOOTE (*Amer. J. Sci.*, 1895, [3], 50, 480—481).—This was found by C. H. Northup, in clay at Borax Lake, California, as regular octahedra, of a dirty white to dark brown colour. Cleavage imperfect; brittle, with uneven fracture; $H = 3.5\text{--}4$. There are regularly arranged enclosures, probably of organic matter. When heated, the mineral blackens, and gives off a burnt odour, with violent decrepitation, owing to mechanically enclosed water; easily fusible. Qualitative analysis shows it to be a double chloride and carbonate of sodium and magnesium, together with traces of phosphoric acid, silica, iron, calcium, and organic matter. Boiling water decomposes the mineral with separation of basic magnesium carbonate. L. J. S.

Nature of Stinkstone (Anthraconite). By WILLIAM SKEY (*Trans. N.Z. Inst.*, 1893, 25, 379—380).—The smell of stinkstone is usually considered to be due to bituminous matter; the author, however, considers that in most cases it is due to hydrogen sulphide, this gas being supposed to be occluded in the free state in the limestone, it not being given off at a red heat. Analysis of a light grey stone, free from bituminous matter, gave

CaCO_3 .	MgCO_3 .	FeO .	CaSO_4 .	Siliceous matter.	Organic matter.	H_2O .	H_2S .	Total.
54.40	0.93	0.21	trace	42.44	0.21	0.89	0.31	99.39

L. J. S.

Optical Properties of Lithiophilite and Triphylite. By SAMUEL L. PENFIELD and JULIUS H. PRATT (*Amer. J. Sci.*, 1895, [3], 50, 387—390).—As iron replaces manganese in the passage from lithiophilite (LiMnPO_4) to triphylite (LiFePO_4), it is shown that there is an increase in the refractive indices, and a gradual change in the size of the optic axial angle, as is seen in the following table, which gives part of the measurements obtained for sodium light.

Locality.	FeO per cent.	β .	$2V$ over b .	Plane of optic axes.
Branchville, Conn.	4.24	1.675	$65^\circ 13'$	(001)
" "	9.42	1.679	62 54	(001)
" "	13.63	1.682	56 4	(001)
Grafton, N.H.	26.58	1.688	—	Uniaxial
Rabenstein, Bavaria ...	35.05	1.702	120 0	(100)

The optically positive mineral from Grafton has for thallium light $2V = 21^\circ 53'$ in the plane (001), and for lithium light $2V = 15^\circ 3'$ in the plane (100). Lithiophilite is optically positive, and the acute bisectrix is perpendicular to (010); the Rabenstein triphylite is optically negative, and the acute bisectrix is perpendicular to (001). On plotting a curve, it is seen that a further increase in the amount of iron would cause $2V$ to become zero again, this time negative, with the optic axis perpendicular to (001); and as the pure compound LiFePO_4 (which is not known) is approached, it may be expected that the optic axis would open out in the plane (010).

L. J. S.

Genesis of Natural Phosphates and Nitrates. By É. J. ARMAND GAUTIER (*Jahrb. f. Min.*, 1895, ii, Ref., 276—279; from *Ann. des Mines*, 1894, [9], 5, 1—53).—After describing the phosphates of the Grotto of Minerva, Dept. Hérault (Abstr., 1893, ii, 419, 577), the author points out that there are three modes of occurrence of commercial phosphates: (1) in igneous rocks and gneisses; (2) in beds and veins, where they have been deposited from solution; (3) nodules and earthy deposits associated with calcium sulphate and carbonate, and nitrogenous organic matter, these being of animal and vegetable origin, and include guano deposits and those of the Grotto of Minerva. Here the ammonium phosphate, formed by the decomposing animal matter, acts on limestone, giving calcium phosphate and ammonium carbonate; the latter with limestone, in connection with nitrifying ferments, producing calcium nitrate. In an experiment, a warm ammoniacal solution of ammonium phosphate acted on an excess of chalk; the product contained 11.28 $\text{Ca}_3(\text{PO}_4)_2$ and 82.78 per cent. of dibasic calcium phosphate, or brushite ($\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$). Similar reactions take place in the presence of clay (Abstr., 1893, ii, 536). The formation of phosphates and nitrates are thus connected; in the presence of sodium chloride, large nitre deposits, such as those of Peru, might be formed.

L. J. S.

Phosphates from Algeria. Phosphatic Rock at Bougie having the Composition of a Superphosphate. By H. MALBOT and A. MALBOT (*Compt. rend.*, 1895, 121, 443—445).—Analyses are given of several Algerian phosphatic deposits; they consist mainly of mixtures of calcium and magnesium phosphates and carbonates, only traces of the phosphates being soluble in water, or in ammonium citrate solution. The deposit at Bougie, however, consists of a hard, red, internal portion, surrounded by a white, friable substance, the composition being as follows.

	Loss at 130°.	Loss at dull redness.	P_2O_5 .	SO_3 .	Soluble SiO_2 .
White substance...	7.93	21.42	33.50	1.51	traces
Red substance....	12.20	9.87	14.42	2.53	0.37
	Fe_2O_3 and Al_2O_3 .	CaO .	MgO .	Insoluble.	
White substance.....	4.33	25.51	0.28	14.00	
Red substance.....	16.35	4.37	0.35	52.07	

In the case of the white substance, 13.29 per cent. of phosphoric anhydride is soluble in water, 8.51 is insoluble in water, but soluble in ammonium citrate solution, and the remaining 11.70 per cent. soluble in dilute acids; in the case of the red substance, 2.03 per cent. is soluble in water, and the remaining 12.39 per cent. is soluble in ammonium citrate solution.

When phosphoric acid is directly precipitated by magnesia mixture in presence of ammonium citrate from solutions containing organic matter, the results are too low. The organic matter, as a rule, is incompletely destroyed by evaporating with nitric acid, and the substance should be heated at dull redness in contact with air. Intermediate precipitation with ammonium molybdate avoids the error arising from the presence of organic matter. C. H. B.

Kentrolite from Långban. By GUSTAV FLINK (*Jahrb. f. Min.*, 1895, ii, Ref., 240; from *Bihang Vet. Akad. Hand. (Stockh.)*, 1891, 16, ii, No. 4).—Black, orthorhombic crystals of kentrolite occur with braunite, richterite, barytes, and calcite at Långban, Sweden. Analysis gave

SiO ₂ .	Mn ₂ O ₃ .	Fe ₂ O ₃ .	PbO.	MnO.	CaO.	Total.	Sp. gr.
17.68	16.59	5.58	55.72	3.05	0.91	99.53	6.068

The formula is given as $R_2''\text{SiO}_4 + R_2'''\text{SiO}_5$, where R'' is Pb: Mn: Ca = 33: 5: 2, and R''' is Mn: Fe = 3: 1. L. J. S.

Thorium and Yttrium Minerals of Norway. By LUDWIG SCHMELCK (*Zeit. angew. Chem.*, 1895, 542—543).—The external characters, blowpipe reactions, action of acids, and approximate thorium and yttrium percentages, are given of the various Norwegian minerals, which are used for the extraction of these oxides for incandescent lights: these minerals are thorite and orangite, æschynite, euxenite, fergusonite, gadolinite, orthite, monazite, xenotime, and keilhauite. The commercial thorite and orangite usually do not contain more than 45 and 60 per cent. of thorium respectively. L. J. S.

Analyses of Beryl. By JAMES S. DE BENNEVILLE (*J. Amer. Chem. Soc.*, 1894, 16, 65—66).—In the following analyses special attention was paid to the alkalis. I, dull yellow, from Fahlun, Sweden. II, apple green, Black Mt., Buncombe Co., N.C. III and IV, light green, Acworth, N.H.

	SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	FeO.	MgO.	CaO.	K ₂ O.	Cs ₂ O.	Na ₂ O.
I.	64.02	16.44	0.68	12.91	0.23	0.50	2.76	—	0.25
II.	66.24	17.64	1.36	11.06	0.09	0.36	0.30	—	0.60
III.	65.23	17.72	1.35	12.37	0.37	0.61	0.35	—	0.53
IV.	66.53	17.11	0.94	12.24	0.20	0.43	0.22	0.12	0.97
	Li ₂ O.	H ₂ O.	P ₂ O ₅ .	Total.	Sp. gr.				
I.	0.05	1.76	0.26	99.86	2.713				
II.	0.14	2.06	0.78	100.63	2.748				
III.	0.06	1.49	0.14	100.22	2.714				
IV.	0.17	1.49	trace	100.45	2.730				

L.

Analyses of the Emerald. By PAUL LEBEAU (*Compt. rend.*, 1895, **121**, 601—603).—An analysis was made of an average sample of about 30 kilos. of emerald from the neighbourhood of Limoges. The emerald was in large, crystallised fragments, and showed, as a rule, little colour; it contained manganese, phosphoric acid, titanous acid, and free fluorine, which have not previously been observed in emeralds from this locality.

SiO ₂ .	Al ₂ O ₃ .	BeO.	Fe ₂ O ₃ .	Mn ₂ O ₄ .	MgO.	CaO.	P ₂ O ₅ .	Loss on ignition.
65.93	16.25	14.27	1.05	0.12	0.58	0.16	0.10	1.44

with traces of alkalis and of TiO₂.

Some of the crystals contain veins of a dark coloured substance, and when powdered, or when treated with concentrated sulphuric acid, evolve a gas which has the odour of ozone. Becquerel and Moissan have shown that the odour of ozone observed in the case of the fluorspar from Quincié, under similar conditions, is due to the presence of free fluorine, which decomposes the moisture of the air. It would follow that the Limoges emeralds contain free fluorine or a perfluoride, and this is confirmed by the fact that the gas evolved by the action of sulphuric acid etches glass.

C. H. B.

Optical Properties of some Compact and Earthy Silicates.

By ALFRED LACROIX (*Compt. rend.*, 1895, **121**, 737—739).—The following ill-defined minerals, which appear to the eye to be compact or earthy, were all found, on examination under the microscope, to show an acute negative bisectrix, with an optic axial angle of varying size, perpendicular, or nearly so, to a good lamellar cleavage; these characters being analogous to those of the micas, it may be assumed that these minerals are monosymmetric: chrome-ochre, glauconite, celadonite, chamosite, berthierine, bavalite, aërinite, talc, meerschaum, clays related to halloysite (severite, lenzinite) and montmorillonite (confolensite, delanouite), and nontronite (pinguite and gramenite).

L. J. S.

Opal, Andalusite, Tourmaline, Sillimanite, Cordierite, Pinguite, and Hoefelite from Bohemia. By FRIEDRICH KATZER (*Tsch. Min. Mitth.*, 1895, **14**, 483—525).—Opal occurs in a pegmatite vein in the gneiss near Pisek, it being shown to have been derived, together with some kaolin, from the felspar. I is the analysis of the yellow opal, sp. gr. 2.294, and II of the bluish-white, sp. gr. 2.313.

	H ₂ O.	SiO ₂ .	Al ₂ O ₃ , Fe ₂ O ₃ .	CaO.	MnO.	MgO.	Alkalis [diff.].	Total.
I.	5.77	84.86	6.56	trace	trace	2.21	[0.60]	100.00
II.	5.35	90.62	3.18	trace	—	1.02	trace	100.17

Both are completely decomposed by hot hydrochloric acid, but only incompletely by aqueous potash, the insoluble portion (22.47 per cent. for the yellow, and 32.88 for the bluish-white) containing, besides opal, small quantities of kaolin, quartz, mica, limonite, hæmatite, psilomelane, felspar, nontronite and chalcedony.

Andalusite, in rose- to hyacinth-red, columnar masses, in a peg-

matite vein near Čejov, gave analysis I for the dark, and II for the light coloured. The powder is rose-red, the colour becoming lighter on ignition. Secondary cordierite is intimately associated with the andalusite. III is the analysis of a very similar andalusite from a pegmatite vein near Sedlitz.

	SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	Loss (H ₂ O).	K ₂ O.	Total.	Sp. gr.
I.	38·15	60·11	1·52	0·99	—	100·77	3·119
II.	38·52	60·59		0·99	—	100·10	
III.	37·34	60·84	1·40	1·27	trace	100·85	3·122

The varying quantity of silica, which is somewhat in excess of that required by the formula $\text{Al}_2\text{O}_3, \text{SiO}_2$, and the presence of water may indicate commencing decomposition.

Tourmaline.—A partial analysis of the black tourmaline, associated with the andalusite of Čejov, gave

H ₂ O.	SiC ₂ .	Al ₂ O ₃ .	FeO.	MnO.	MgO.	CaO.	Total.
2·24	38·01	31·72	12·47	trace	2·05	small quantity	86·49

It is intimately associated with what appears to be secondary muscovite. Sp. gr. 3·166.

Sillimanite occurs in the cordierite rock of Humpoletz in places where the effects of pressure on the rock are evident. The fine, colourless needles form a silver-white to yellowish aggregate, which has a silky lustre, and a hardness as low as 2 to 4. Analysis I is of the finely fibrous variety; II, of the more coarsely crystalline, which is closely associated with quartz.

	SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	CaO.	Loss on ignition.	Total.	Sp. gr.
I.	37·11	60·54	trace	0·38	2·40	100·43	3·153
II.	43·12	55·81	—	0·42	0·99	100·34	—

Although the excess of silica in II is best explained by the presence of quartz, it may, perhaps, indicate an approach to $\text{Al}_2(\text{SiO}_4)_3$ (wörthite?).

Cordierite, from the cordierite rock of Humpoletz, gave

SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	FeO.	MgO.	MnO.	Loss (H ₂ O).	Total.	Sp. gr.
50·13	32·11	2·24	6·37	8·47	0·32	0·99	100·63	2·696

This gives the formula $\text{H}_2\text{O}, 6(\text{Mg}, \text{Fe})\text{O}, 6(\text{Al}_2, \text{Fe}_2)\text{O}_3, 15\text{SiO}_2$; or, if the water be neglected $(\text{Mg}, \text{Fe})_2(\text{Al}, \text{Fe})_4\text{Si}_5\text{O}_{18}$.

Pinguite, of a yellowish-green colour, occurs in earthy masses with kaolin and sandy iron-ochre in a weathered schist at Spaniow, near Taus; it is supposed to have been produced by the action of sulphuric acid, derived from pyrites, on felspar. The mineral, on a fresh fracture, is greenish, and has a fatty appearance. $\text{H} = 1$; sp. gr. 2·727. It fuses with difficulty to a black, magnetic slag; it is completely decomposed by concentrated sulphuric acid. The mean of two analyses of air-dried material gave

Loss on ignition (H ₂ O).	SiO ₂ .	Fe ₂ O ₃ (and a little FeO).	Al ₂ O ₃ .	CaO.	Total.
22·48	41·33	35·10	0·75	1·01	100·67

At 110°, 16·53 per cent. of water is given off; at 250°, 17·09 per cent. Formula, $\text{Fe}_2\text{O}_3, 3\text{SiO}_2, 5\text{H}_2\text{O}$, or $2\text{Fe}_2\text{O}_3, 6\text{SiO}_2, 3\text{H}_2\text{O} + 8\text{Aq}$.

Hoeferite, this new mineral from Kiitz, near Rakonitz, has much the same mode of occurrence and origin as the pinguite described above. It is earthy and of a siskin-green colour with fatty lustre, $H = 1-3$. It is difficultly fusible to a black, magnetic slag; it is only partly decomposed by strong sulphuric acid, and not at all by hydrochloric acid or by aqueous potash. The material was purified by means of dilute acid, and after being air dried, gave on analysis

SiO_2 .	Fe_2O_3 (and a little FeO).	Al_2O_3 .	Loss on ignition.	Total.	Loss at 120°.	Sp. gr.
36·14	45·26	1·11	18·15	100·66	0·99	2·27
35·88	46·64		18·20	100·72	3·79	2·41

Formula $2\text{Fe}_2\text{O}_3, 4\text{SiO}_2, 7\text{H}_2\text{O}$. The points in which the mineral differs from nontronite, pinguite, and other chloropals are given. Schrauf's analysis of chloropal from Mugrau is reduced to a mixture of hoeferite and $\text{CaO}, 3\text{SiO}_2, 4\text{H}_2\text{O}$. L. J. S.

Zeolites of the Syenite near Dresden. By E. ZSCHAU (*Abh. Ges. Isis*, 1894, (1893), 90—105).—The modes of occurrence of the various zeolites found in connection with the syenite of the Plauenscher Grund are described in detail. Brick-red, granular laumontite gave analysis I; this red mineral does not lose water and crumble, as the white does. Of the eight analyses given for analcite, II is of the massive, red mineral, and III of the white and crystalline. Red radiated natrolite gave IV; sp. gr. 2·243—2·266.

	SiO_2 .	Al_2O_3 .	Fe_2O_3 .	CaO .	Na_2O .	H_2O .	Total.
I. Laumontite.....	53·88	20·73	trace	9·28	1·97	13·96	99·82
II. Analcite (red)....	58·16	20·43	little	0·37	11·43	8·79	99·18
III. Do. (white)...	57·32	20·90	trace	0·31	11·45	9·18	99·16
IV. Natrolite.....	48·04	26·17	trace	0·96	13·96	9·91	99·04

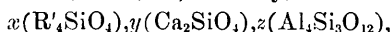
L. J. S.

Isomorphism of the Felspars (Albite-Anorthite). By FR. WALLERANT (*Compt. rend.*, 1895, 121, 740—741).—As the optic axial angles calculated for the felspars, on the assumption that they are isomorphous mixtures of albite and anorthite, do not agree with the observed values, it is considered that the albite and anorthite molecules are chemically combined. L. J. S.

The Leucite-nepheline Group. By CARL F. RAMMELSBERG (*Ber. Akad. Berlin*, 1892, 543—561).—The minerals here considered form two dimorphous groups, represented by the cubic leucite and the hexagonal nepheline. Most are orthosilicates, but leucite, pollucite (and nepheline partly, as here shown) are metasilicates; these and other differences in the composition and formulæ of these isomorphous groups find an analogy in the felspars. The formulæ here given for pollucite, leucite, kaliophilite, eucryptite, and Doelter's artificial soda-nepheline are the usual ones. In *nepheline*, where the

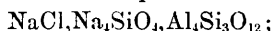
silica is in excess of the orthosilicate formula, the ratio Al : Si = 1 : 1.4 is assumed, giving the formula $R_{14}Al_{14}Si_{16}O_{60}$, or, as K : Na is often as 1 : 5, $6(Na_2Al_2Si_2O_8), K_2Al_2Si_2O_{12}$. This combination of an orthosilicate (soda-nepheline) with another salt (the metasilicate leucite) is what occurs in the sodalite group. This formula also explains the observed alteration of leucite into sanidine and nepheline as follows: $13R_2Al_2Si_4O_{12}$ (leucite) = $R_{14}Al_{14}Si_{16}O_{60}$ (nepheline) + $6R_2Al_2Si_6O_{18}$ (orthoclase).

Cancrinite (with davyne) is written as an isomorphous mixture of carbonate and silicate, as was done for the very similar artificial silico-carbonate (Abstr., 1887, 12), namely,

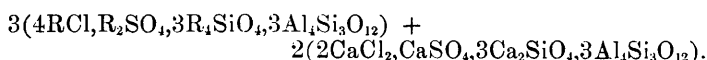


where R' represents Na and H, and Si represents Si and C in varying amounts; $x = 2z$.

Sodalite is written as the isomorphous mixture



here the ratio Cl : Si is 1 : 4, it may also be 1 : 3. Formulæ on the same lines are given for hâüyne, nosean, and the hexagonal microsommitte, the last being



Lazulite, from Brögger and Bäckström's analysis, is deduced as $NaCl, 4NaS_2, 10Na_2SO_4, 10Na_4Al_4Si_4O_{16}$, with part of the sodium replaced by calcium; deducting the artificial ultramarine from this, the hâüyne formula is arrived at.

L. J. S.

Ilvaite, Harmotome, Opal, Danaite, Scheelite, Chromiferous Muscovite, Gersdorffite, Nickeliferous Pyrrhotite from Canada.

By G. CHRISTIAN HOFFMANN (*Report Geol. Survey, Canada*, 1892, 5, ii, R, 1—72).—*Ilvaite*, iron-black, associated with calcite, tremolite, and andradite, from Barclay Sound, Vancouver Island; sp. gr., 3.859.

SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	FeO.	MnO.	CaO.	MgO.	H ₂ O.	Total.
29.81	0.16	18.89	32.50	2.22	13.82	0.30	1.62	99.32

Harmotome, small crystals on calcite, from O'Connor, Ontario; sp. gr., 2.39.

SiO ₂ .	Al ₂ O ₃ .	BaO.	CaO.	K ₂ O.	Na ₂ O.	H ₂ O.	Total.
46.36	17.16	21.18	2.25	?	?	14.54	101.49

Opal, common, white, or greenish, from basaltic breccias at Savona Mtn., B.C.; sp. gr., 2.012, after ignition, 2.083. It is nearly all soluble in caustic potash, the residue consisting of SiO₂ 0.76, Al₂O₃ 0.23, Fe₂O₃ 0.26, CaO 0.35, MgO 0.23, alkalis ? 0.09 = 1.92 per cent. On ignition, there is a loss of 7.00 per cent. of water; of this, 3.25 per cent. is lost over sulphuric acid; the material dried over acid gains 6.75 per cent. in a moist atmosphere, and the original material gains 3.28 under similar conditions or when immersed in water. After ignition, water is not re-absorbed.

Danaité, massive, steel-grey, associated with nickeliferous pyrrhotite at Graham, Ontario; sp. gr., 5·983. An analysis by R. A. A. Johnston gave, after deducting, 4·77 per cent. of quartz,

As.	S.	Fe.	Co.	Ni.	Sb.	Au.	Total.
42·22	18·84	33·32	4·09	0·93	0·60	trace	100·00

Scheelite, in pale wine-yellow crystals, associated with hæmatite, pyrrhotite, pyrites, and quartz at Marlow, Quebec, gave on analysis by Johnston,

WO ₃ .	CaO.	Fe ₂ O ₃ .	SiO ₂ .	Total.	Sp. gr.
79·90	19·37	0·79	0·29	100·26	6·059

Chromiferous muscovite, massive, bright emerald-green, from Matawatchan, Renfrew Co., Ontario, gave on analysis by F. G. Wait; sp. gr., 2·93.

SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	Cr ₂ O ₃ .	MnO.	CaO.	MgO.	K ₂ O.	Na ₂ O.	H ₂ O.	Total.
43·72	35·51	2·94	1·26	0·26	4·46	1·36	8·88	0·39	3·68	102·46

Gersdorffite, massive, or as crystals (octahedra or cubo-octahedra), steel-grey, associated with niccolite, pyrrhotite, &c., at Denison, Ontario; sp. gr., 6·231. Analysis by Johnston gave, after deducting 13·55 per cent. of quartz,

As.	S.	Ni.	Fe.	Co.	Cu.	Total.
46·96	16·71	26·32	7·90	2·01	0·10	100·00

Nickeliferous Pyrrhotite.—The results of the examination of 30 nickel ores are given; most of these are pyrrhotite with an average of about 2 per cent. of Ni (varies from a trace to 4·13 per cent.); cobalt is absent, or present only in traces (in one case there is 0·17 per cent.). Numerous analyses are given of various ores, waters, &c., in the report.

L. J. S.

The Wide-spread Occurrence of Barium and Strontium in Silicate Rocks. By WILLIAM F. HILLEBRAND (*J. Amer. Chem. Soc.*, 1894, 16, 81—82).—Attention is drawn to the fact that the detailed rock analyses made in the laboratory of the United States Geological Survey often show the presence of barium and strontium, usually below 0·1 per cent. of each, but sometimes a little more, as in some rocks from Montana and Colorado (compare next page).

L. J. S.

Banded Gabbros of Skye. By Sir ARCHIBALD GEIKIE and J. J. HARRIS TEALL (*Quart. Journ. Geol. Soc.*, 1894, 50, 645—660).—Analyses, by J. H. Player, are given of various portions of the banded gabbros of Drunmairidhne. I is of a light coloured band mainly composed of labradorite, also with augite, uraltic hornblende, and magnetite. II, a dark band composed of augite, magnetite, and labradorite. III, a thin, ultrabasic band mainly composed of augite and magnetite. The titanium is present in the magnetite, but not as an intergrowth of ilmenite.

	SiO ₂ .	TiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	FeO.	FeS ₂ .	Mn oxide.	CaO.	MgO
I.	52.8	0.5	17.8	1.2	4.8	—	—	12.9	4.8
II.	40.2	4.7	9.5	9.7	12.2	0.4	0.4	13.1	8.0
III.	29.5	9.2	3.8	17.8	18.2	0.4	0.3	10.0	8.7

	Na ₂ O.	K ₂ O.	Loss on ignition.	Total.	Sp. gr.
I.	3.0	0.5	1.2	99.5	2.91
II.	0.8	0.2	0.5	99.7	3.36
III.	0.2	0.1	1.0	99.2	3.87

This variation is supposed to be due to the intrusion of a heterogeneous magma.

L. J. S.

Igneous Rock of Yogo Peak, Montana. By WALTER H. WEEB and LOUIS V. PIRSSON (*Amer. J. Sci.*, 1895, [3], **50**, 467—479).—The massive, granular, igneous rock of Yogo Peak, which consists mainly of augite and orthoclase, shows a progressive differentiation along the axis of the mass; at one end of the rock is a syenite (anal. I), and as the ferro-magnesian minerals and the basicity increase, it passes through the new types *yogoite* (anal. II) and *shonkinite* (anal. III). Apatite, sphene, iron ore, hornblende, oligoclase or andesine, and biotite are always present, but in varying amounts in the different types; in the syenite, there is a little quartz, and in the shonkinite a little olivine. Yogoite is defined as a rock having about equal amounts of orthoclase and augite (including other ferro-magnesian minerals), there being a predominance of orthoclase in syenite, and of augite in the shonkinite type; the last name was first given by the authors (*Bull. Geol. Soc. Amer.*, 1895, **6**, 400—422) to a rock from Square Butte, Montana (anal. IV). The extreme members of this series would be sanidinite and pyroxenite.

	SiO ₂ .	TiO ₂ .	Al ₂ O ₃ .	Cr ₂ O ₃ .	Fe ₂ O ₃ .	FeO.	MnO.	MgO.	CaO.	BaO.
I.	61.65	0.56	15.07	trace	2.03	2.25	0.09	3.67	4.61	0.27
II.	54.42	0.80	14.28	trace	3.32	4.13	0.10	6.12	7.72	0.32
III.	48.98	1.44	12.29	trace	2.88	5.77	0.08	9.19	9.65	0.43
IV.	46.73	0.78	10.05	—	3.53	8.20	0.28	9.68	13.22	n.d.

	SrO.	Na ₂ O.	K ₂ O.	Li ₂ O.	H ₂ O (at 110°).	H ₂ O (above 110°).	P ₂ O ₅ .	Total.
I.	0.10	4.35	4.50	trace	0.26	0.41	0.33	100.15
II.	0.13	3.44	4.22	trace	0.22	0.38	0.59	100.19
III.	0.08	2.22	4.96	trace	0.26	0.56	0.98	99.99
IV.	n.d.	1.81	3.76	trace	1.24		1.51	100.97

L. J. S.

Olivine-andesite of Banks Peninsula, N.Z. By R. SPEIGHT (*Trans. N.Z. Inst.*, 1893, **25**, 367—375).—This rock shows in analysis I a comparatively large silica percentage considering the large amount of olivine present; augite is present only in small quantity; sp. gr., 2.68. The porphyritic labradorite felspar gave II; sp. gr., 2.719.

	SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ + FeO.	CaO.	MgO.	Na ₂ O.	K ₂ O.	Loss on ignition.	Total.
I.	55.12	20.41	7.74	5.35	2.75	3.80	2.50	3.13	100.80
II.	55.3	26.3	1.8	11.4	—	5.30	trace	—	100.1

L. J. S.

Tridymite-trachyte of Lyttelton, New Zealand. By PATRICK MARSHALL (*Trans. N.Z. Inst.*, 1894, **26**, 368—387).—This rock occurs in the volcanic system of Banks Peninsula; it is of a very light colour, with large porphyritic crystals of plagioclase, and in vesicles numerous clear, glassy crystals of tridymite; ferro-magnesian minerals are rare or absent, but magnetite is abundant, and there is no interstitial glass. I and II are the extremes, as regards silica percentage, of the five analyses given; sp. gr., 2.351—2.415. Calculated from the analyses, there must be 29 per cent. of free silica, which is supposed to exist as tridymite in the ground mass; 29.95 per cent. of the rock is dissolved by boiling aqueous soda, but of this 15.05 per cent. is alumina. III gives the analysis of the felspar, which includes a narrow border of orthoclase round the plagioclase. Analysis of the associated basic and intermediate volcanic rocks are given.

	SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	FeO.	CaO.	MgO.	K ₂ O.	Na ₂ O.	H ₂ O.	Total.
I.	73.07	13.75	2.55	—	3.27	0.99	2.46	4.60	—	100.69
II.	71.09	15.45	1.05	0.34	3.25	0.89	2.35	4.81	0.07	99.75
III.	60.56	22.05	—	—	7.25	—	3.54	7.93	—	101.33

I and II have traces of MnO, and I trace of P₂O₅. L. J. S.

Meteorite from Moonbi, Tamworth, N.S.W. By JOHN C. H. MINGAYE (*Journ. and Proc. Roy. Soc., N.S.W.*, 1893, **27**, 82—83).—This meteorite, weighing 29 lbs., gave on analysis

Fe.	Ni.	Co.	Cu.	Sn.	Cr.	C (graphite).	C (combined).
91.350	7.886	0.564	trace	0.003	trace	0.068	trace

SiO ₂ .	S.	P.	O.	Total.	Sp. gr.
0.039	nil	0.217	trace	100.127	7.833

L. J. S.

The Cherokee and El Capitan Meteorites. By EDWIN E. HOWELL (*Amer. J. Sci.*, 1895, [3], **50**, 252—254).—*The Cherokee meteorite* was found in 1894 near Cherokee Mills, Cherokee Co., Georgia; weight, 15½ lbs. Widmanstätten figures are strongly marked; analysis I by H. N. Stokes. *The Losttown meteorite*, found in 1868 in the same county, is of different appearance and composition, having only 3.36 per cent. of nickel.

	Fe.	Ni.	Co.	Cu.	Si.	P.	S.	C.	Total.
I.	91.96	6.70	0.50	0.03	trace	0.11	0.01	trace?	99.31
II.	90.51	8.40	0.60	0.05	trace	0.24	trace	—	99.80

The El Capitan meteorite was found in 1893 on the northern slope of the El Capitan range, New Mexico; weight about 61 lbs.

Analysis II by H. N. Stokes. It is suggested that this may be the "fiery ball" seen in the neighbourhood in 1882. L. J. S.

Meteorites. By HENRI MOISSAN (*Compt. rend.*, 1895, **121**, 483—486).—Meteoric iron from Kendall Co., Texas, was found to contain amorphous carbon, but neither graphite nor diamond; a specimen from Newstead, in Scotland, contains amorphous carbon and graphite, but no diamond; one from the Sierra de Déesa, in Chili, contains a small quantity of graphite which seems to have been subjected to moderate pressure, but neither diamond nor amorphous carbon; another from Toluca-Xiquipilso, in Mexico, contains no carbon at all; the iron from Novy-Urej, Krasnoslobodsk, Russia, was found to contain amorphous carbon and black diamond, as Jeroféeff and Latchinoff have already stated.

A further examination of the iron from Cañon Diablo, confirms the author's earlier statement, that this meteorite contains black diamonds, and it is the only meteorite in which the author has found amorphous carbon, graphite, and diamond together. C. H. B.

Water from Lake Corangamite, Victoria. By ANDREW W. CRAIG and N. T. M. WILSMORE (*Australian Assoc. Adv. Sci.*, 4th Report, 1893 [1892], 270—271).—Sp. gr. = 1.035; analysis gave in parts per 1000,

Ca.	Mg.	K.	Na.	SO ₄ .	Cl.	Br.	Total bases. as sulphates.
0.063	1.272	0.387	16.145	0.758	27.312	0.102	57.276

Hydrogen sulphide and carbonic anhydride were also present. The water was specially examined for rare alkalis, but only lithium, potassium, and sodium were found in the concentrated mother liquor.

L. J. S.

Water from Nashville, Illinois, and from the Soap Lake, Washington. By GEORGE STEIGER (*Bull. U.S. Geol. Survey*, 1893, No. 113, 113).—Water from the "American Carlsbad Spring," at Nashville, Illinois, contained in one million parts 4262.31 parts of solids consisting of: SiO₂, 0.29; SO₄, 39.76; CO₃, 26.80; Cl, 0.57; Al₂O₃, 0.08; Ca, 10.02; Mg, 6.51; Na, 15.97 = 100.00. Hypothetical combinations: NaCl, 0.95; Na₂SO₄, 48.15; MgSO₄, 9.01; MgCO₃, 16.47; CaCO₃, 25.05; Al₂O₃, 0.08; SiO₂, 0.29 = 100.00.

Water from the Soap Lake, Washington, contained in one million parts 28194.57 parts of solids consisting of: SiO₂, 0.40; SO₄, 15.47; CO₃, 34.13; Cl, 12.50; Ca, trace; Mg, 0.04; Na, 37.27; H (bicarbonate), 0.19 = 100.00. Hypothetical combinations: NaCl, 20.61; Na₂SO₄, 22.89; Na₂CO₃, 40.22; NaHCO₃, 15.65; MgH₂C₂O₆, 0.23; SiO₂, 0.40 = 100.00. The water is strongly alkaline, and contains some organic matter. L. J. S.

Analysis of Water from Ojo Caliente, New Mexico. By WILLIAM F. HILLEBRAND (*Bull. U.S. Geol. Survey*, 1893, No. 113, 114).—A thermal spring near Taos; sp. gr. 1.00273 at 18.4°. In parts per million were found: SiO₂, 60.2; SO₄, 151.0; PO₄, 0.2; CO₃, 2153.5; B₂O₃, 4.2; Cl, 231.4; F, 5.2; Fe₂O₃, 1.6; Al₂O₃, 0.5; Ca, 22.8;

Sr, 1.4; Mg, 9.5; K, 31.4; Na, 995.1; Li, 3.4 = 3671.4. The hypothetical combinations are: LiCl, 0.62; KCl, 1.76; NaCl, 9.01; $\text{Na}_2\text{B}_4\text{O}_7$, 0.16; Na_2SO_4 , 6.59; Na_2CO_3 , 54.49; $\text{Ca}_3\text{P}_2\text{O}_8$, 0.01; CaF_2 , 0.32; CaCO_3 , 1.27; SrCO_3 , 0.07; MgCO_3 , 0.98; SiO, 1.78; Fe_2O_3 , 0.05; Al_2O_3 , 0.01; CO_2 (bicarbonate), 22.88 = 100.00. Also traces of arsenic, nitrates, iodine (?), barium, and ammonia. No organic matter, titanium, bromine, manganese, or sulphides. L. J. S.

Bituminous Mineral Waters containing Ammonia. By F. PARMENTIER (*Compt. rend.*, 1895, **121**, 644—645).—Many of the mineral waters in the neighbourhood of Clermont contain small quantities of volatile bituminous matter recognisable only by its smell and taste, and all these waters contain ammonia. The water of a spring at Grassion, from the bituminous limestone, has the following composition per litre:—Residue at 180° , 4.500; total CO_2 , 4.870; Cl, 0.075; SO_3 , 0.016; SiO_2 , 0.050; CaO, 0.330; MgO, 0.155; K_2O , 0.026; Na_2O , 2.036; Li_2O , 0.001; Al_2O_3 , 0.004; NH_3 , 0.006; no traces of iron, arsenic, nitrates, or non-volatile organic matter.

Three other springs contained the following quantities of ammonia per litre:—Médecins, 0.0010; la Vallière, 0.0002; artesian well, 0.0040. The water of the spring at *Puy de la Poix* contains as much as 0.0454 gram of ammonia per litre. There is some evidence that part of the nitrogen is present in the form of organic amines.

C. H. B.

Physiological Chemistry.

Respiration in Marine Invertebrates. By HORACE M. VERNON (*J. Physiol.*, 1895, **19**, 18—70).—Observations relating to the respiratory exchanges in many of the lower marine invertebrates are described. An appendix treats of the composition of the gases and salinity of sea water.

The respiratory activity of these animals is small as compared with that of fishes. The more lowly the animal, as a rule, the greater is the increased effect produced by a rise of temperature, moreover, the respiratory activity varies inversely as the size of the animal. Captivity produced opposite effects in different animals. The respiratory quotients are higher, as a rule, than in warm-blooded animals, and generally become greater than unity on asphyxiation; in one case (*Amphioxus*) it rose to 4.45. This is probably due to the rapid onset of decomposition.

Calculated on the amount of solid in their bodies, the respiration of these lower marine animals is enormous, usually greater than in man. Thus *Cestus* and *Salpa* contain respectively only 0.24 and 0.26 per cent. of solids; other transparent animals 0.4 to 0.6; *Amphioxus* 12.8, and the fish *Heliosus*, 22.3. During captivity, pelagic animals rapidly get smaller, and the respiratory quotients, as a rule, increase. The rhythm of the *Medusa rhizostoma* is not affected by temperature to

so great an extent as the respiratory activity. The rhythm rapidly decreases during activity.
W. D. H.

Gas Formation in the Human Stomach. By ERNST WISSEL (*Zeit. physiol. Chem.*, 1895, **21**, 234—252).—Six cases were investigated, and very exhaustive tables are given of the analyses of the gases removed from the stomach, and also of those which formed in the stomach contents after removal. G. Hoppe-Seyler's method of analysis was employed. The fermentation and the presence of sarcinae are by no means interdependent. The gases found were those of swallowed air, *plus* a large excess of carbonic anhydride and of hydrogen.
W. D. H.

Exchange of Liquids between Blood and Tissues. By J. B. LEATHES (*J. Physiol.*, 1895, **19**, 1—14).—The conclusions to which the experiments recorded lead are: Changes in the osmotic pressure of the blood are compensated, with extreme rapidity, by the transfer of liquid from tissues to blood, or from blood to tissues, when the kidneys are excluded from the circulation. There is no evidence that the vessel walls play other than the part of a passive membrane in this interchange of liquids. They cannot be said to have the power of actively regulating the composition of the circulating blood. The osmotic pressure of the lymph from the thoracic duct is always slightly above that of the blood. This slight difference is not affected by alterations in the osmotic pressure of the blood, and is more easily accounted for by metabolism in the tissues than by any active function of the vessel walls.
W. D. H.

Initial Rates of Osmosis of certain Substances in Water and in Liquids containing Albumin. By W. S. LAZARUS-BARLOW (*J. Physiol.*, 1895, **19**, 140—166).—The osmometer used, a new one, is described and figured. The conclusions arrived at are.

(1) The ratio between the initial rates of osmosis of glucose, sodium chloride, and urea in equimolecular solutions is not the same as the ratio between their final osmotic pressures, or the ratio between the differences of their freezing points and that of water. The practical bearing of this conclusion is that it is impossible to state, from a determination of their freezing points, that one solution is hypertonic, isotonic, or hypotonic as regards another solution of a different composition at pressures within the limits possible in the animal body. This can only be determined by experiment in each case.

(2) The ratio between the initial rates of osmosis of glucose, sodium chloride, and urea in equimolecular solutions differs according as the membrane is composed of peritoneum or copper ferrocyanide. The importance of the membrane as a factor has been previously insisted on by Graham and L. Meyer.

(3) In the case of the peritoneal membrane, the initial rate of osmosis of the three substances named is diminished by the presence of even small quantities of albumin.

(4) With the same membrane in watery or albuminous solutions,

the initial rate of osmosis of glucose is greater than that of sodium chloride; that of urea being the smallest. W. D. H.

Intravascular Injection of Peptone. By ERNEST H. STARLING (*J. Physiol.*, 1895, 19, 15—17).—The present experiments do not confirm Gley's statement (*Arch. de Physiol.*, 1895, 711) that in dogs, after ligation of the portal lymphatics, the injection of "peptone" has no effect on the blood. Gley's results are explained by supposing that he dealt with an accidental aggregation of immune dogs. W. D. H.

Absorption of Iron Salts. By H. W. F. C. WOLTERING (*Zeit. physiol. Chem.*, 1895, 21, 186—233).—In attempting a solution of this vexed question, the method adopted was to estimate the amount of iron in the liver and other organs, not in the urine, as in the work of many previous investigators. The animals used were mice, dogs, and rabbits. In some control experiments, manganese was given instead of iron, the sulphates being the salts used. Microscopic investigation showed a greater amount of iron in those animals to which iron had been given; this was confirmed by quantitative analysis. The iron of the liver is contained in part in the nucleo-proteid of that organ. In the blood of the animals, the amount of hæmoglobin and the number of red corpuscles increases. W. D. H.

Effect of Feeding Cows with Whale and Herring Meal, especially as regards Milk Production. By JOHN SEEBLIEN (*Landw. Versuchs-Stat.*, 1895, 46, 259—308).—Experiments were made in which groups of 10 carefully selected cows were fed with and without whale meal. In the preliminary period (of one month), in which both groups were fed alike, the food was as follows:—Turnips (80), straw chaff (90), hay (40), rape cake meal, linseed cake meal, and malt germs (each 10 kilos.). During the next period (10th January to 1st March, 1894), whale meal was given to the second group in increasing amounts (5 to 15 kilos.), whilst the food of the first group remained much the same as in the preliminary period. During the third period of three weeks, the food of both groups was the same (without whale meal). The effect of whale meal was to raise the yield of milk by 6 per cent. or more during the period in which it was given; but there was no after effect. It made no difference whether 0·5 kilo. of whale meal was given or 1·5 kilo. (the cake being in this case reduced by 1 kilo.). The percentage of fat was not altered by the whale meal when this was given as additional food, but was lowered when an extra quantity was given in the place of cake. The absolute amount of fat was increased during the first period of whale meal feeding, but sank during the last period (with increased quantity of whale meal) to the amount produced in the preliminary period. As regards live weight, there was practically no difference in the two groups.

The results of very numerous experiments made in Denmark indicate that the composition of milk remains constant with different foods, and, in the author's experiments, very abnormal amounts of protein produced merely a lowering of the percentage of fat. It

seems probable that the increase in fat observed when cows are turned out to grass, is due rather to the more natural way of living than to the difference in the composition of the food. The experiments with herring meal were chiefly to ascertain whether any taste was imparted to the milk and butter. The results showed that the meal had no effect either on the taste, or on the keeping qualities of the milk and butter; and the chemical examination of the butter produced from cows fed with whale meal, showed no alteration in the Wollny numbers or in the Köttstorffer numbers; and there was no depression in the iodine numbers, showing that there is no direct migration of the whale meal oil into the milk.

The evidence obtained from agriculturists as regards the taste and keeping properties of the butter is in favour of whale meal.

N. H. J. M.

Digestibility and Nutritive Value of Pumpkin Seed Cake and Buckwheat Grain. By A. WICKE and HUGO WEISKE (*Landw. Versuchs-Stat.* 1895, 46, 371—382).—Two full grown sheep were fed for three periods of 16 days with (I) hay (1 kilo.), (II) hay (900 grams), and air-dried pumpkin seed cake (100 grams), and (III) hay (800 grams), and air-dried buckwheat (200 grams) respectively. During the second eight days of each period, the fæces and urine were collected and examined. The following numbers show the percentages of the different constituents (1) of pumpkin-seed cake (sheep No. 1), and (2 and 3) of buckwheat (sheep Nos. 1 and 2), which were digested.

	Dry matter.	Organic matter.	Protein.	Fat.	Crude fibre.	N-free extract.	Ash.
1.	83·15	88·55	84·73	104·63	118·76	42·74	56·19
2.	74·22	74·55	79·73	92·37	40·21	77·56	62·04
3.	67·37	67·65	69·76	108·87	7·94	74·03	50·93

The high results obtained in the case of fat and crude fibre (over 100), are ascribed to the difficulties and defects of the method. The results show, however, that pumpkin seed cake is a highly digestible food, about 85 per cent. of the protein and the whole of the fat being digested. As regards the experiments with buckwheat, the results (2) obtained with sheep No. 1 are the more trustworthy. They show that in buckwheat all the constituents (except the crude fibre) are very digestible, in part more digestible than those of the cereals. It is possible, however, that the employment of both foods in larger quantities might give less favourable results; in the case of pumpkin seed, owing to the high percentage of fat.

N. H. J. M.

Pigments of the Pieridæ. By F. GOWLAND HOPKINS (*Proc. Roy. Soc.*, 1894, 57, 5—6).—The wing scales of the group of butterflies known as the white Pieridæ, contain uric acid; those of the yellow Pieridæ contain, as their pigment, a yellow derivative of uric acid, which the author has obtained synthetically by heating uric acid with water in sealed tubes at high temperatures. This yellow pigment the author terms *Lepidotie acid*, and its constitution is still under investigation.

J. J. S.

Constancy of the Freezing Point of Milk and other Organic Liquids. By J. WINTER (*Compt. rend.*, 1895, **121**, 696—698).—Cryometric observations show that milk and blood serum are equimolecular, and their molecular concentration is the same in all the animals examined. This seems to be true, also, of other liquids derived from animal organisms. The constancy of the freezing point of milk affords a valuable means of testing its purity; its spontaneous alterations rapidly lower the freezing point, whilst the addition of water raises it. Experiments with milk from various sources show that the values of Δ , the reduction in the freezing point, vary between 0.55 and 0.57, whilst the values for the number of gram-molecules per 100 grams of water, n , vary between 0.297 and 0.308. In a large majority of cases, including all the specimens of human milk, the value of Δ was 0.55, and that of n 0.297. The corresponding values for blood serum from several different animals vary between exactly the same limits.

From these results, it is possible to consider the effects of various solutions on living blood, independently of the nature of the dissolved substance. If the molecular concentration of the solution is not equal to that of the serum, it will produce either a dissolution of the suspended red and white corpuscles, or a precipitation of dissolved fibrin and other constituents. It follows that the blood corpuscles and fibrin must be regarded as having the function of regulating the molecular concentration of the blood serum, just as undissolved crystals maintain a saturated solution at the point of saturation.

C. H. B.

Vernix Caseosa. By W. G. RUPPEL (*Zeit. physiol. Chem.*, 1895, **21**, 122—133).—This secretion of the foetal skin contains 35 per cent. of water, and 14 per cent. of substances soluble in ether. The remainder consists of proteid and ash, in which calcium, magnesium, sodium, potassium, and phosphoric anhydride, but only traces of chlorine were recognised.

Attention was, however, particularly directed to the ethereal extract. In it glycerol and oleic and palmitic acids were found, but the chief interest centres round the discovery of ischolesterol in it. In this, the secretion is similar to the fat of sheep's wool.

W. D. H.

Absence of Sugar from Normal Urine proved by a New Method. By SIR GEORGE JOHNSON (*Pharm. J. Trans.*, 1895, [3], **25**, 603—605).—If 4 c.c. of normal urine is placed in a test tube of about half an inch diameter, an equal volume of a saturated aqueous solution of picric acid added, and then 2 c.c. of liq. potassæ (P.B.), an orange-red colour instantly appears as a result of the incipient reducing action of creatinine at the ordinary temperature. If the liquid be heated and kept at the boiling point for about a minute, the colour deepens, and appears bright red through the test tube, held up to the light. If an aqueous solution of glucose, containing 2 grains to the ounce, be treated in like manner, the liquid will be so dark that no light will be visible across the full diameter of the tube. The solution of glucose ceases to give any coloration when it is diluted beyond 1 part in 10,000: but the creatinine reaction continues until the dilu-

tion reaches 1 part in 200,000. The extreme delicacy of the latter reaction affords a method of detecting a small quantity of glucose in the presence of creatinine by comparing the colorations produced by known quantities or dilutions.

R. R.

Poisonous Effects of Acetylene. By NESTOR GRÉHANT (*Compt. rend.*, 1895, **121**, 564—566; by MARCELLIN BERTHELOT, *ibid.*, 566; and by HENRI MOISSAN, *ibid.*, 566).—A mixture of 20 vols. of acetylene, prepared from calcium carbide, 20·8 vols. of oxygen, and 59·2 vols. of nitrogen was breathed by a dog for 35 minutes without any marked disturbance, and 100 c.c. of the blood was found to contain 10 c.c. of acetylene. With 40 vols. of acetylene, the proportion of oxygen remaining the same, a dog died in less than an hour, owing to failure of the heart's action, and 100 c.c. of blood contained 20 c.c. of acetylene. With 79 vols. of acetylene and 21 vols. of oxygen, the poisonous effects were still more strongly marked. It follows that acetylene may be fatally poisonous when present in proportions as high as 40 per cent. by volume.

A mixture of coal gas with air and oxygen containing 20·8 per cent. of the latter and 1 per cent. of carbonic oxide was nearly fatal to a dog after it had been breathed for about 10 minutes, and 100 c.c. of the dog's blood contained 27 c.c. of carbonic oxide. It follows that acetylene is much less poisonous than ordinary coal gas.

Berthelot, in some experiments made many years ago, in conjunction with Claude Bernard, found that acetylene, when present to the extent of a few per cents. by volume, is without injurious effects on birds. The poisonous properties often attributed to this gas, as prepared by the older methods, are probably due to the presence of carbonic oxide or hydrogen cyanide.

Moissan finds that when acetylene is prepared from pure calcium carbide, and is purified by being liquefied, it has a very pleasant, ethereal odour, and can be breathed in small quantity without evil effects. If, however, the calcium carbide has been prepared from coal and impure lime, it may contain calcium sulphide and phosphide, and the acetylene prepared from it then has a very disagreeable odour.

C. H. B.

Constitution of Heteroxanthine and its Physiological Action.

By MARTIN KRÜGER and GEORG SALOMON (*Zeit. physiol. Chem.*, 1895, **21**, 169—185).—From 10,000 litres of human urine, 13 grams of xanthine, 12·5 grams of paraxanthine, and 7·5 grams of heteroxanthine were obtained.

The author's experiments show that heteroxanthine is a methyl-xanthine, having the constitution $\begin{array}{c} \text{NH}\cdot\text{CH}\cdot\text{C}\cdot\text{NMe} \\ | \\ \text{CO}\cdot\text{NH}\cdot\text{C}=\text{N} \end{array} > \text{CO}$, for it yields carbonic anhydride (2 mols.), carbonic oxide (1 mol.), ammonia (3 mols.), and sarcosine (1 mol.), when hydrolysed by acids, whilst further methylation converts it into caffeine.

On injection into frogs, the principal symptom is increased contractility of the voluntary muscles; in mammals, similar convulsions are seen. After injection, it cannot be found in the urine, and is therefore probably almost completely oxidised in the body.

W. D. H.

Derivatives of Hydrastine and Narcotine. By EDMUND FALK (*Virchow's Archiv*, 1895, **142**, 360—379).—Methylhydrastamide produces, in both cold and warm-blooded animals, peripheral paralysis. In larger doses, it paralyses the heart; it dilates the vessels, lowers the blood pressure, and causes death by cessation of respiration.

Methylhydrastimide acts on the muscular tissues producing paralysis preceded by cramps; even in small doses it weakens the heart. There is dilatation of vessels, and death occurs, as in the former case.

Methylnarcotamide produces a narcotic state by acting on the cerebrum, and there is paralysis of a peripheral nature. Very large doses are necessary to affect the heart; there is fall of blood pressure. Respiration is first quickened, then becomes slower, and finally ceases.

Methylnarcotimide is a narcotic, but paralysis is incomplete and accompanied by a stage of muscular cramp; on the heart, however, its paralysing action is more marked. It is a local anæsthetic at the seat of application. There is fall of blood pressure. Respiration rises during the convulsions, but in the narcotic stage falls, and finally ceases.

W. D. H.

Chemistry of Vegetable Physiology and Agriculture.

Physiology of Yeast and the Importance of Selected and Pure Cultures for Wine Fermentation. By HERMANN MÜLLER (*Bied. Centr.*, 1895, **24**, 695—698; from *Jahresber. deut. schweiz. Versuchs. Stat. Wädenswil*, 1894, **3**, 73).—A comparison of the number of yeasts and fungi (given in millions per hundred grapes) on healthy and burst grapes shows an enormous increase in the latter, especially in the number of yeast-like fungi, as compared with that of wine yeast. The relation of wine yeasts to others is most favourable in dry autumns, and high-hanging grapes are better in this respect than those near the ground. The different wine yeasts vary very much in activity. Rapid production of violent fermentation forms the best means of suppressing injurious fungi and bacteria, both by quickly utilising the oxygen present in the liquid and replacing the air by carbonic anhydride, and also by the poisonous action of carbonic anhydride on many fungi. Too violent fermentation may be disadvantageous, by causing frothing over, and especially by producing too high a temperature. Frothing is produced by the yeast rising to the surface and by the separation of fine particles from the liquid, which subsequently float and form a thin layer.

A number of yeasts from various wine districts were examined as regards their power of fermenting sugar.

The bouquet of wines is produced by fermentation from substances in the grape juice which possess no odour. Apart from the bouquet, the yeasts produce tastes and odours peculiar to themselves (just as

Penicillium causes the characteristic mouldy odour), which, of course, alter the bouquet more or less.

In cultivating the yeasts, fresh, sterilised grape-must is most suitable, currant, apple, and pear must are less, and artificial solutions still less suitable. Addition of ammonium chloride increases the production.

By means of pure cultivations of yeast, the process of wine-making is shortened, the taste and odour are decidedly purer and free from faults; the wine will also keep better. Cider, so made, has a greater resemblance to wine from grapes. The general employment of pure cultivations is only a matter of time.

N. H. J. M.

The Sugar that forms in the Auto-digestion of Yeast. By ERNST L. SALKOWSKI (*Zeit. Biol.*, 1895, **32**, 468—472).—M. Cremer suggests that the sugar which the present author previously described as formed on the auto-digestion of yeast, and as being levorotatory, does not exist, but that peptone accounts for the rotation.

Renewed experiments show that no peptone or proteose is present, and that the leucine found will only account for a small part of the rotation. The identification of the sugar is not, however, yet effected.

W. D. H.

Measurement of the Reducing Power of Pure Yeasts. By NASTUKOFF (*Compt. rend.*, 1895, **121**, 535—536).—The author measures the reducing power of yeasts by the degree of blackening produced in a 10 per cent. solution of cane sugar, to which has been added 5 grams per litre of Gastine's saline mixture (*Compt. rend.*, 1889, **109**, 479), the calcium sulphate being replaced by magnesium sulphate and some basic bismuth nitrate being added. The same race of yeast gives practically constant results, but different races show different reducing powers. Comparison of the degree of darkening with the quantity of alcohol produced, or of carbonic anhydride evolved, shows that these two forms of protoplasmic activity have no direct connection.

The liquid containing the bismuth may be placed in a tube immersed in a liquid containing no bismuth, but otherwise similar in composition, the two being separated by goldbeater's skin and mixing only by diffusion. Instead of measuring the darkening of the bismuth solution, advantage may be taken of the fact that the sulphide gives a yellow tint with the nitrites that are formed simultaneously, that this coloration is not affected by boiling, and that its intensity can be measured.

The five yeasts examined, showed reducing powers in the following order, the most powerful reducer being placed first: (1) wine yeast from Champagne; (2) wine yeast from Portugal; (3) *Saccharomyces pastorianus*; (4) *Saccharomyces apiculatus*; (5) beer yeast from Brussels.

C. H. B.

Fermentation of Cellulose. By V. OMELIANSKI (*Compt. rend.*, 1895, **121**, 653—655).—*Bacillus amylobacter*, which has hitherto been regarded as the special ferment of cellulose, is really a collective

species, including a large number of different butyric ferments. None of these has, so far, shown any marked power of decomposing pure cellulose. The special microbe of cellulose fermentation can be isolated by the method of elective cultures. Swedish filter paper and chalk are placed in a solution of potassium phosphate, magnesium sulphate, and ammonium sulphate, with a trace of ooze of the Nêva. The flasks are hermetically closed and kept at 30—35°; fermentation is somewhat rapid, and the paper becomes yellowish, transparent, and gelatinous, and finally dissolves, some of the chalk dissolving at the same time. The ferment is found on the paper, and not in the liquid; it is very thin, 6 to 7 μ long, and 0.2—0.3 μ broad, and forms very round spores, 1 μ in diameter. Further cultivations on potato are necessary, in order to obtain the bacillus quite pure. C. H. B.

Ethylic Alcohol from the Fermentation of *Asphodelus ramosus* and *Scilla maritima*. By G. RIVIÈRE and BAILHACHE (*Compt. rend.*, 1895, **121**, 659—662).—The tuberous roots of *Asphodelus ramosus*, which grows abundantly in the wild state in Algeria, were cut up and extracted with warm water by diffusion. The solution was boiled, allowed to cool, mixed with 2 per cent. of lime, allowed to remain for 48 hours, filtered, and the excess of calcium precipitated with sulphuric acid; after removal of the calcium sulphate, the "solution" was limpid, and slightly amber coloured. The exhausted cossettes were pulped, mixed with 2 per cent. of sulphuric acid, boiled in order to completely saccharify the starches, filtered, mixed with lime in quantity sufficient to leave an excess of 2 per cent., and allowed to remain for 48 hours. It was then filtered, neutralised with sulphuric acid, and, after separation of the calcium sulphate, mixed with the solution obtained in the first stage.

The mixed solutions were sterilised by successive ebullitions with two days' interval, cooled, and mixed with pure yeast from the white wine of Burgundy. Fermentation begins almost immediately, and is complete in four or five days, distillation yielding a liquid with an alcoholic strength of 50° to 55°. The alcohol has the agreeable bouquet due to the yeast, and is free from the disagreeable odour that has hitherto characterised alcohol from the asphodel.

Scilla maritima, which also grows abundantly in the wild state in Algeria, when treated in a similar manner, yields an alcohol resembling wine brandy, and with the bouquet characteristic of the particular yeast.

The alcohol from *Scilla* has a flavour somewhat inferior to that of the alcohol from *Asphodelus*, and contains a higher proportion of aldehyde. Both, however, are free from furfuraldehyde, and contain only slight traces of higher alcohols. C. H. B.

Assimilation of Elementary Nitrogen by Plants. By JULIUS STOKLASA (*Landw. Jahrb.*, 1895, **24**, 827—863).—The results of observations made with lupins (*Lupinus angustifolius*) grown in a field, indicated that the plants without nodules grew as well as those with nodules. The soil was a poor, loamy sand (nitrogen = 0.023 per cent.). The total nitrogen of both plants was practically the same, but (at

the flowering period) was differently distributed. In the plants without nodules, there was more nitrogen in the stems and leaves; in those with nodules, the roots were richer in nitrogen than the roots without nodules. The average weight of the nodules was 0.74 gram when fresh, 0.117 gram when dry, and the dry matter contained 4.5 per cent. of nitrogen.

Four series of pot experiments were made, in which lupins were grown: (1) in ignited sand, maintained in a state of sterilisation; (2) in the same sand, with the addition of a few grams of lupin soil; (3) in sandy soil (N = 0.0065 per cent.); and (4) in the sandy soil, microbe seeded with lupin soil. There were 12 or 16 pots (each with one plant) in each series, but in the following table the results of 10 pots are taken together in each case. The nitrogen supplied includes in each case (1) the nitrogen of the 10 seeds sown (0.069 gram), (2) nitrogen as ammonia (0.099 gram), and as nitrates (0.100 gram), supposed to have been possibly absorbed from the air, and (3) the nitrogen of the lupin soil added (= 0.152 gram) to the 10 pots.

	Dry produce (10 plants).	Nitrogen.		
		Supplied.	In produce.	Gain.
1. Ignited sand sterilised....	27.86	0.268	0.459	0.191
2. " " inoculated ..	64.85	0.420	1.995	1.575
3. Sandy soil not sterilised ..	66.40	0.268	2.394	2.126
4. " " inoculated	63.85	0.420	2.510	2.090

In series (1) there was thus some fixation under conditions of sterilisation, and without nodule formation, that is, without symbiosis, whilst in series (2), in which well formed nodules were produced, fixation was much increased. In series (3) the surface of the soil was covered with algæ; incompletely developed nodules were found on the roots of four plants; but in the above table only plants free from nodules are included. In series (4), in which a number of well formed nodules were produced, there was rather less fixation than in series (3).

As regards the nitrogen of the sandy soil of series (3) and (4), the percentage increased from 0.0065 at the commencement to 0.0098 in series (3), and 0.0104 in series (4) at the conclusion, whilst the total soil nitrogen in each pot (14 kilos. of sand) rose from 0.91 gram to 1.372 and 1.456 gram respectively; there was thus a gain of nitrogen due to the bacteria and algæ. The results show that under conditions of sterilisation, nitrogen assimilation is very feeble, whilst soil inoculation increases it eight fold. In non-sterilised soil, in which algæ and bacteria increase the nitrogen required for the first development of the plants, lupins without nodules assimilate nitrogen to the same extent as lupins with nodules.

An examination of the nodules of *Lupinus luteus* showed that they contained no ammonia, and only traces of nitric acid, the latter dis-

appearing at the period of ripeness. The percentage of total nitrogen in the dry matter of roots and nodules at (1) the flowering period, (2) the period of fruit formation, and (3) at the period of complete ripeness are given below; also the percentage of nitrogen as proteids, amides, and asparagine in the nodules at the first and third periods.

Period.	Nitrogen in roots.	Nitrogen in nodules.			
		Total.	As proteids.	As amides.	As asparagine.
1	1.64	5.22	3.99	0.35	0.34
2	1.84	2.61	—	—	—
3	1.42	1.73	1.54	0.15	traces

The pure ash of the roots (4.55 per cent.), and the nodules (6.32 per cent.) had the percentage composition.

	K ₂ O.	Na ₂ O.	CaO.	MgO.	Fe ₂ O ₃ .	P ₂ O ₅ .	SO ₃ .	SiO ₂ .
Roots..	14.52	26.88	16.87	11.73	1.08	9.82	15.84	3.59
Nodules	20.86	22.74	10.71	12.35	1.19	14.94	12.25	3.01

In order to ascertain whether the absence of light has any effect on the nodules as well as on the leaves, a number of well-developed, flowering lupin plants were kept in the dark for 13 days; by this time the plants had become yellow, and were taken up along with similar plants, kept under ordinary conditions, and examined. The results are given in percentages of the dry substances of (1) leaves and nodules of normal plants, and (2) of the plants kept in the dark.

	Leaves.				Nodules.			
	Nitrogen.		Aspara- gine.	Lecithin.	Nitrogen.		Aspara- gine.	Lecithin.
	Total.	Proteïn.			Total.	Proteïn.		
1 ..	3.29	2.87	0.49	1.24	4.99	3.96	1.37	1.12
2 ..	3.47	1.80	4.19	0.63	3.11	1.47	4.98	0.53

The average weight of the single nodules was (1) 0.1184, (2) 0.0806 gram.

The results of these experiments confirm the view generally held regarding the production of asparagine in plants in absence of light, not only in the leaves but also in the root nodules; they also show that in the nodules the living plasma with the bacteria does not support independent processes of nitrogen assimilation.

The following amounts of oxalic acid and hexoses (reckoned as glucose) were found in the dry nodules.

	Oxalic acid.	Hexoses.
Nodules of the normal plants	2.06	6.33
„ of the plants kept dark	1.06	5.89

It is concluded that assimilation takes place in the leaves, and that the amides migrate from the leaves to the root nodules, where they interact with glucose to produce proteids, these forming the nutritive medium for bacteria.

Experiments were made on nitrogen fixation by a non-leguminous plant—buckwheat. The plants were grown in iron vessels holding 14 kilograms each; five seeds were sown in each pot. There were four series, each comprising eight (or four) pots, as follows:—(1) Ignited sand, with minerals; (2) sandy soil ($N = 0.0065$ per cent.), not sterilised; (3 and 4) same as (1) and (2) respectively, with addition of ammonium nitrate (0.5 gram to each pot). The following results were obtained.

No. of series.	Number of plants.	Dry produce.	Nitrogen.			
			In seeds sown.	As NH_4NO_3 added.	In produce.	Gain.
1	37	3.04	0.0176	—	0.0712	0.0536
2	40	20.43	0.0190	—	0.603	0.5840
3	16	41.24	0.0076	0.7	1.258	0.5504
4	16	58.56	0.0076	0.7	1.816	1.1084

The average gain of nitrogen in these, and a number of similar experiments made from 1890 to 1894, was (1) 0.138, (2) 1.378, (3) 3.385, and (4) 6.09 grams for 100 plants. The gain in the soil itself was in series (2) from 0.0065 to 0.020; series (4) to 0.039 per cent. There was about the same gain in similar soil kept without vegetation. In series (1) and (3), a trace of nitrogen was found in the sand at the end of the experiment.

The results obtained with series (1) indicate a gain of nitrogen under conditions of sterilisation, but in such small quantity that it may have been derived from the combined nitrogen of the air. In series (2), the results obtained with the plants and with soils free from vegetation show that the plants must have fixed free nitrogen. In sterilised sandy soil, series (3), with ammonium nitrate, the assimilation was greatly increased, whilst in series (4) there was over forty times as much nitrogen assimilated (by the plants) as in sterilised sand.

Further experiments were made in which buckwheat was grown in the ignited sand, to which sterilised horn meal was added (so as to make the percentage of nitrogen correspond with that of the soil) as well as 0.5 gram of ammonium nitrate. The gain of nitrogen in the plants was practically the same as that already obtained in series (3). It is, therefore, seen that in sterilised soil containing an excess of

nitrogenous food, the plant never develops as well as in non sterilised soil, in presence of algæ and bacteria.

It is concluded that nitrogen fixation by buckwheat increases with the development of the leaves and roots; that in sterilised soil and without combined nitrogen there will be no considerable fixation; that in presence of nitrates in excess, if under conditions of sterilisation, nitrogen assimilation never reaches the maximum, as compared with plants grown in non-sterilised soils, and that Hellriegel's theory of nitrogen fixation by Leguminosæ alone in symbiosis is wrong. Whilst agreeing with Frank, that free nitrogen is assimilated by the living protoplasm of the cells of green leaves and roots, the author maintains that the bacteria of the soil play a very essential part in the process.

N. H. J. M.

The Mineral Food of Lower Fungi. By HANS MOLISCH (*Bied. Centr.*, 1895, 24, 635; from *Bot. Centr.*, 1894, 167).—Iron is necessary for fungi, and cannot be replaced by manganese, cobalt, or nickel. In opposition to Nägeli, it is stated that magnesium is indispensable, and cannot be replaced by metals of the alkaline earths or of the zinc group (Zn, Be, Cd), cadmium being poisonous even in very dilute solutions. Calcium is not necessary for the lower fungi (or, as has recently been shown, for algæ); this is the one remarkable difference as regards the requirements of fungi as compared with the higher plants; the other nine elements (C, H, O, N, S, P, K, Mg, Fe) being equally necessary for both.

N. H. J. H.

Physiological Studies on Hops. By J. BEHRENS (*Bied. Centr.*, 1895, 24, 635; from *Bot. Centr.*, 1894, 178).—The rhizome differs from the above-ground sprouts in colour, absence of leaves, and also in being much thicker, its fleshy consistence indicating its character as reservoir. It is produced only by external influences. The percentage composition of the dry rhizome branches (free from sand), cut in the spring, is as follows.

N.	Proteïds.	Non-proteïn (as asparagine).	Directly reducing sugar.	Invert sugar (as cane).	Ether extract.	Ash.
3·46	14·28	5·57	9·62	8·58	2·08	7·08

N. H. J. M.

Formation of Indigo in Plants of the Order Indigofera. By C. J. VAN LOOKEREN and P. J. VAN DER VEEN (*Landw. Versuchs-Stat.*, 1895, 46, 249—258; compare *Abstr.*, 1895, i, 96).—The extract of the leaves of the indigofera shows an alkaline reaction with litmus and with rosolic acid, an acid reaction with phenolphthaleïn. When the leaves are "fermented" with dilute (0·5 to 1 per cent.) acids, solutions are obtained which yield indigo under the influence of atmospheric oxygen and behave similarly to the solutions obtained by reducing ordinary indigo, precipitating with dilute acid, extracting with chloroform, and taking up the residue with water. Such a solution cannot be obtained from pure indigotin.

Indigotin-white, together with indirubin-white, and other products formed from indican under the influence of enzymes in absence of air,

behave differently, as regards solubility in water and chloroform and in the readiness with which they are oxidised, from indigo-white, either in the pure state or mixed with indifferent substances. Indigo-blue containing so-called "indigo-brown" is slightly soluble in presence of free alkali, whilst if indigo-red is present it is also soluble in alcohol; this explains why acid extracts contain indigo-white in solution.

N. H. J. M.

Occurrence of Carotene. By SCHRÖTTER-KRISTELLI (*Bied. Centr.*, 1895, **24**, 709—710; from *Bot. Centr.*, 1895, **61**, 33).—The yellow dye was found dissolved in oil, in the outer cell layers of the seed covering of *Azelia Cuanzensis*. The yellow, yellowish-red, and vermilion dyes, known under various names, which occur in plants and animals, mostly belong to a homologous series for which the name *lipoxanthin* series is proposed. The dyes are always united to fatty substances, are insoluble in water, are not fluorescent, give a blue colour when treated with sulphuric acid, absorb the violet rays of the spectrum, and are readily decomposed by light and heat.

In plants, an entirely different group of yellow dyes occurs. These are dissolved in the sap, and give a red or brown colour with sulphuric acid.

The lipoxanthin colours are terpene-like substances, which absorb oxygen without being destroyed as long as the protoplasm has sufficient vigour. It is probable that by continued reducing action, cholesterol yields yellow, and finally green, colouring matters (chlorophyll); whilst, by oxidation, chlorophyll would yield yellow dyes, and finally cholesterol.

N. H. J. M.

The Nitrogenous Constituents of Young Green Plants of *Vicia Sativa*. By ERNST SCHULZE (*Landw. Versuchs.-Stat.*, 1895, **46**, 383—397).—In the course of an investigation on the composition of etiolated seedlings of the vetch, *Vicia sativa*, as compared with normal green plants, Prianischnikow (Abstr., 1895, ii, 124) identified asparagine with certainty, whilst the other compounds were not obtained in sufficient quantity for separation. The author has now succeeded in identifying leucin in six-weeks old plants. Amidovaleric acid and phenylalanin, which occur along with leucine in etiolated seedlings, could not be detected in the green plants. As regards organic bases, both betaine and choline were separated, whilst the results of both the author's and Prianischnikow's experiments make it probable that guanidine is present in small amount.

In nine-weeks old plants, asparagine and xanthine substances (nuclein bases) were found, but not vernin; betaine and a very small quantity of a base which seemed to be choline were also found.

Betaine seems not to belong to those constituents of seeds which are consumed during germination. Choline occurs in etiolated plants in greater amount than in the ungerminated seeds, and is probably produced in the decomposition of lecithin in absence of light. Guanidine is doubtless present in much smaller quantity in green than in etiolated plants.

N. H. J. M.

The Seeds of *Nephelium Lappaceum* and the Fats contained therein. By MAX BACZEWSKI (*Monatsh.*, 1895, **16**, 866—880).—The percentage composition of the ground seed of *Nephelium lappaceum* is as follows. Water, 5·87; fat, soluble in ether and petroleum, 35·07; ether extractive matter, insoluble in petroleum, 3·00; ash, 1·95; albumin, 8·89; crude fibre, 6·90; starch, 25·63; sugar, 1·25. The fats consist of the triglycerides of arachic and oleic acids, together with a very small quantity of the triglyceride of stearic acid.

G. T. M.

Chemical Composition of Capsicum. By BÉLA VON BITTÓ (*Landw. Versuchs-Stat.*, 1895, **46**, 309—327; compare Abstr., 1893, ii, 546).—The oil extracted by ether from the seeds of capsicum becomes green when kept in a vacuum over sulphuric acid. Its sp. gr. = 0·91095 at 15°; iodine number, 119·5; Köttsdorfer number = 187·2. It contains C = 76·35, H = 11·35 per cent. The mean of two determinations of free fatty acids (mainly palmitic, with some stearic and oleic acids) in the oil was 2·75 per cent., or 0·64 and 0·70 per cent. in the fresh and dried seeds respectively. The glycerides calculated as olein (which was the chief constituent) amounted to 24·06 per cent. in the dry seeds. When the oil is long exposed to air, an intense green colour is produced owing to the presence of a small quantity of chlorophyll.

In separating the free fatty acids from the glycerides by extracting once or twice with light petroleum, it was noticed that the acids had a sharp, burning taste, due to the presence of an active substance which was separated in small quantity. This forms white crystals, very readily soluble in chloroform and ether, rather soluble in light petroleum, sparingly soluble in absolute alcohol, and insoluble in water. It has an acid reaction, dissolves in alkaline solutions, but is precipitated by carbonic anhydride. It has an extremely burning taste, and when heated, gives off vapours which violently attack the mucous membrane.

The average amount of lecithin in the dried seeds was found to be 1·82 per cent., when determined directly by Schulze and Steiger's method.

Fresh analyses of the seeds were made, as before, by Henneberg's method, but the results do not differ much from those previously obtained (*loc. cit.*), except in the case of the nitrogen-free extract (29·64) and the crude fibre (21·23 per cent. on dry matter). The crude fibre was redetermined by Schulze's method (*Landw. Versuchs-Stat.*, **39**, 283); the average result was 30·50 per cent. The nitrogen-free extract then amounts to 20·19 per cent., consisting in part only of carbohydrates. There seems to be only a trace of a true carbohydrate (either dextrose or a substance which, when hydrolysed, gives dextrose); pentoses are present in greater amount, whilst galactose, mannose, starch, and cane sugar, &c., could not be detected.

By means of 1·5 per cent. aqueous potash, a new carbohydrate, termed *capsicum seed mucilage*, was extracted from the seeds. It is insoluble in water, merely swelling. With iodine, a green coloration is produced which rapidly becomes blue. Zinc chloride and potassium

iodide give no reaction. After boiling with acids, it readily reduces Fehling's solution. It contains pentose and probably galactose groups.

New analyses of the placenta are given, and also the averages of these and the earlier results (*loc. cit.*). The pure ash of the placenta has the following percentage composition.

K ₂ O.	Na ₂ O.	CaO.	MgO.	Fe ₂ O ₃ .	P ₂ O ₅ .	SO ₃ .	SiO ₂ .	Cl.
66.06	4.44	4.70	3.97	0.88	8.75	8.32	3.72	2.89

Alumina and manganese were found in traces in the ash.

N. H. J. M.

Constituents of the Tissues of Fungi. By ERNST WINTERSTEIN (*Zeit. physiol. Chem.*, 1895, **21**, 134—151; compare Abstr., 1894, ii, 425; 1895, i, 80, 199, 323, and 493; also Gilson, Abstr., 1895, i, 323, ii, 323 and 408).—This paper is mainly a *résumé* of work published elsewhere.

J. J. S.

Constituents of the Cell Membranes of various Cryptogams. By ERNST WINTERSTEIN (*Zeit. physiol. Chem.*, 1895, **21**, 152—154; compare Schulze, Abstr., 1894, ii, 250).—For his investigation, the author has used two species of fern, *Aspidium filix mas.* and *Asplenium filix fem.*, and several species of moss belonging to the *Bryaceæ* family. Cellulose preparations were made from the cell membranes, and then the products obtained by hydrolysis with sulphuric acid were investigated; from each preparation a syrup was obtained, which consisted mainly of *d*-glucose mixed with a small quantity of mannose.

J. J. S.

Proteïds of Cotton Seeds. By THOMAS B. OSBORNE and CLARK G. VOORHEES (*J. Amer. Chem. Soc.*, 1894, **16**, 778—785).—This is mainly an account of preliminary experiments. The oil-free cotton seed meal was first extracted with water, and the solution, after dialysis, yielded 0.75 per cent. of proteose-like matter. When further extracted with 10—20 per cent. solution of common salt, the meal yielded a larger amount of globulin (15.83 per cent.), which in properties and composition is remarkably similar to the vegetable vitellin of flax, hemp, &c.; no other globulins soluble in sodium chloride solution could be isolated. The authors term the globulin which is soluble in salt "*edestin*," since it occurs in so many important food stuffs. The meal was further treated with aqueous potash, and yielded other proteïd matter, which, however, could not be obtained in a pure state. The residue, after treatment with potash, also contains a notable quantity of nitrogen.

J. J. S.

Injury to Plants by Nitrogen acids. By F. JOSEF KÖNIG and EMIL HASELHOFF (*Bied. Centr.*, 1895, **24**, 610—611; from *Landw. Jahrb.*, 1894, **23**, 1031).—Experiments made on young trees showed that 1 part of hyponitrous acid (calculated as N₂O₄) in 20,000 parts of air (or 0.05 gram in 1 cubic metre) is injurious. As air contains 0.00003 gram of nitrous acid per cubic metre, the air to be injurious

must contain 2,000 times as much as is generally present. The limit within which nitrogen acids become injurious is between those of hydrogen chloride (1 : 15,000 vol. according to Christel) and sulphurous acid (1 : 54,000 vol. according to Freitag).

The effects produced on leaves by nitrogen acids are similar to those of sulphurous and hydrochloric acids—brown or yellow spots or edges.
N. H. J. M.

Effect of Strychnine on Plant Development. By R. OTTO (*Bied. Centr.*, 1895, **24**, 711; from *Naturw. Wochenschr.*, 1894, No. 51, 625).—The addition of strychnine phosphate to four weeks old beans, grown in sand and in humus soil respectively, greatly retarded the growth of the plants growing in sand. The plants flowered, but did not produce normal fruit. In soil, the plants were slightly retarded, had an almost normal colour, and produced a quantity of normal fruit. More than 10·5 grams of strychnine salt was added to 2 kilograms of soil during the eight weeks the experiment lasted. On extracting the soils with water, no strychnine was found, the poison having been destroyed by the soil. In soils which were saturated with a solution of strychnine from the commencement, the germination of beans was considerably delayed; two plants in soil, however, developed comparatively normally, whilst those in sand decayed.

N. H. J. M.

Black Siberian Lupins. By BERNHARD SCHULZE (*Bied. Centr.*, 1895, **24**, 614—615; from *D. Landwir.*, 1895, No. 30, 175).—Black lupins are said to be unusually poor in alkaloids, so that it is not necessary to destroy the alkaloids before feeding. A number of samples of imported black lupins were found to contain in nearly every case more alkaloids than are found in the native yellow, white and blue lupins, and complete analyses of black and yellow lupins, the results of which are given, show that the black are not better than the German varieties either as regards nutritive qualities or amount of alkaloids. Black lupins are very rich in alkaloids, and probably contain the poison which causes the disease known as lupinose.
N. H. J. M.

Effect of Different Manures on the Composition and Combustibility of Tobacco. By HARRY J. PATTERSON (*Bied. Centr.*, 1895, **24**, 662—663; from *Agric. Science*, 1894, **8**, 329).—The experiments were made in five of the chief tobacco growing districts of Maryland. The amount of total ash depends chiefly on the soil, and only slightly on manuring, but it was found that potassium chloride raised the percentage of ash most. The amounts of lime and magnesia are influenced by manuring, but still more by the character of the soil, whilst the amount of chlorine is more influenced by manuring.

Tobacco which burns well generally contains much sand and silica; the combustibility increases with the amount of lime and magnesia, but there seems to be no relation between combustibility and amount of phosphoric acid or of crude fibre. The quality of tobacco is largely influenced by the character of the previous growth. In Maryland, land growing pines is found most suitable; chestnut land comes

next, whilst land on which oaks and hickory are growing is unsuitable for tobacco, and is planted first with *Andropogon virginicum*, followed by pines. The effect of these plants on the cultivation of tobacco is explained by its requirements as regards potash and chlorine. The relation between chlorine and potash in the red pine is 1 : 1·3, in *Andropogon* 1 : 2·5, in chestnut 1 : 14·4, in oak 1 : 50·0, and in hickory 1 : 63·0. The beneficial plants withdraw much chlorine from the soil, the others much potash. N. H. J. M.

Composition of Rice imported into France. By BALLAND (*Compt. rend.*, 1895, 121, 561—564).—Decorticated rice from the principal localities (Burmah, Carolina, India, Japan, Java, Piedmont, Saigon [Cochin China]) shows percentage compositions varying between the extremes quoted below.

	Water.	Nitrogenous matter.	Fat.	Amyloïds.	Cellu- lose.	Ash.
Maximum....	16·00	8·82	0·75	81·35	0·42	0·58
Minimum	10·20	5·50	0·15	75·60	0·18	0·42

Crude rice contains a higher proportion of nitrogenous and fatty substances and ash, the limits being as follows.

	Water.	Nitrogenous matter.	Fat.	Amyloïds.	Cellulose.	Ash.
Minimum....	11·20	6·18	1·85	73·85	0·93	1·20
Maximum....	13·30	9·05	2·50	75·60	2·38	2·20

In refined rice, the acidity lies between 0·032 and 0·062, and the sugar between 0·15 and 0·50, the values in the case of crude rice being 0·043—0·087 and 0·56—0·90 respectively. There is no connection between the size of the grains and the proportion of nitrogenous matter. Rice has more value as a food than is commonly supposed. The Cochin China rice, although the grains are small, contains as much nitrogenous matter and phosphatic ash as some wheats, and rather more fat. The process of decorticating, especially by machinery, greatly reduces the proportion of fat, nitrogenous matter, and ash, and the loss is still higher if the grains are polished.

C. H. B.

Are Nitrates indispensable for the Growth of Plants? By OTTO PIETSCH and J. VAN HAARST (*Landw. Versuchs-Stat.*, 1895, 46, 357—370; compare Abstr., 1893, ii, 385).—The experiments now described were similar to the earlier ones; the nitrifying bacteria were destroyed, and the nitrates present in the soil extracted with water. In 1892, wheat was grown in soil containing 0·105 per cent. of nitrogen, and in the same soil, with addition of ammonium sulphate (corresponding with 1·05 gram and 0·53 gram of nitrogen) and of sodium nitrate (1·05 gram of nitrogen) respectively. The total yield (grains and straw) with the larger amount of ammonium sulphate was less than where no nitrogen was applied; with the smaller amount of ammonium salt, the yield was about the same as without any application, whilst with nitrate, the yield was largely increased. In 1893, experiments were made with oats. The application of nitrates again

gave a much higher yield than the ammonium salts. The application of both potassium and sodium chlorides in conjunction with ammonium salts resulted in a considerably increased production of dry matter as compared with that obtained under the influence of ammonium salts alone; moreover, the yield was practically the same with the larger and smaller amounts of ammonium salts, whereas without the chlorides, considerably less total produce was obtained with the larger than with the smaller amount of ammonium salt. Similar results were obtained (again with oats) in 1893. The question how the sodium and potassium chlorides act has not been studied, but results obtained by Pagnoul (*Abstr.*, 1895, ii, 130) indicate some interaction in the soil beneficial to the plants.

N. H. J. M.

Assimilation of the Nutritive Matters of the Soil by Plants.

By F. JOSEF KÖNIG and EMIL HASELHOFF (*Bied. Centr.*, 1895, **24**, 687—691; from *Landw. Jahrb.*, 1894, **23**, 1009).—Two artificial soils were made, in which the constituents were partly in a physically combined (absorbed), and partly in a chemically combined, state. The percentage composition was as follows.

	Sand.	Clay.	Humus.	Fe ₂ (HO) ₆ .	Al ₂ (HO) ₆ .	Si(HO) ₄ .	Zeolite.
A.	84.1	10.0	2.5	2.5	0.7	0.2	0.0
B.	82.0	10.0	2.5	3.0	0.3	0.2	2.0

The absorptive powers of the two mixtures were tested by Zalomanoff and Pillitz's process, with nutritive solutions of different strengths. In the case of mixture A, a greater absolute as well as percentage amount was absorbed from stronger than from weaker solutions. In the second mixture B, the absorptive power for lime, magnesia, and potash was increased by the presence of zeolite, and the double strength of the nutritive solution caused greater absorption only in the case of lime. Generally $\frac{1}{7}$ to $\frac{1}{4}$ of the lime, 0 to $\frac{1}{3}$ of the magnesia, and $\frac{1}{5}$ to $\frac{1}{2}$ the potash applied were absorbed. Soda and sulphuric acid were only absorbed in traces, whilst the phosphoric acid was completely absorbed.

Vegetation experiments were made, in which barley followed by horse beans were grown in the artificial soils, with and without application of further nutritive matter. The nutritive substances were applied (1) entirely in a soluble form (2, 3, and 4) in both soluble and insoluble form in varying proportions, and (5) in an insoluble form. It was found that whilst the gramineous plant (barley) gave a yield in nearly direct relation to the amount of soluble nutritive matter applied, the yield of leguminous plant (horse bean) was rather in relation to the total amount of nutritive matter than amount of soluble matter. Lime seems to influence the growth of leguminous plants more than potash under otherwise similar nutritive conditions.

The actual amounts of nutritive matter in the soluble and insoluble forms which were taken up by the plants are given in tables.

N. H. J. M.

Composition of Native and Cultivated Soils. Effect of Continuous Cultivation on their Fertility. By HARRY SNYDER (*Minnesota Stat. Bull.*, 1893, No. 30).—Analysis of about 150 Minnesota soils, both cultivated and uncultivated, were made, the surface soils being sampled to a depth of about 9 inches, or until a change of colour was noticed. The most important soils are the deep black soils of the Red River Valley, containing 0.35 to 0.4 per cent. of nitrogen which, by continuous cultivation for 12 or 15 years, has been reduced to 0.2—0.3 per cent. Small spots of alkali soils sometimes occur; these are most benefited by deep ploughing, drainage, and the application of stable manure. "Gumbo" soils are heavy soils consisting of very fine particles less than 0.01 inch in size, and free from true sand. They are rich in potash.

By the continuous, exclusive growth of grain crops for 10—15 years, the amount of humus in the soil is reduced to one-third or one-half, the soil, from loss of organic matter, losing its power of retaining water, and thus becoming subject to drying out.

Soils rich in humus contain more available phosphoric acid than poor soils, and produce more carbonic anhydride, which acts as a solvent on the mineral matter, and thus aids the roots in taking up food. In order to keep up the supply of organic matter in the soil, a system of rotation and application of stable manure is recommended. Artificial manures will then be unnecessary. In some cases where, for instance, the surface soil is rich in nitrogen and phosphates, the corresponding subsoil rich in potash and lime, the good qualities of both surface and subsoil would be utilised by a rotation of crops.

N. H. J. M.

Citrate Solubility of the Phosphoric acid of Basic Slag. By WILHELM HOFFMEISTER (*Landw. Versuchs-Stat.*, 1895, 46, 399—405).—The results of the experiments described indicate that the citrate solubility of the phosphoric acid depends on the amount of lime and silica present, and on the fineness, both as regards the total amount of fine meal, and also the degree of fineness.

Fineness is rendered more easy to obtain mechanically by the presence of large amounts of lime and silica. The value of basic slag depends essentially on the greater or less possibility of the production of tetrabasic calcium phosphate in the fused substance, and on its fineness.

N. H. J. M.

Phosphate Manuring. By VON LIEBENBERG (*Bied. Centr.*, 1895, 24, 663—664; from *Mitteil. Ver. Förd. Versuchswesens Oesterreich*, 1894, 9, 125—128).—The object of the experiments, which will be continued for some years, is to ascertain whether yearly applications of soluble phosphates may with advantage be substituted by one very heavy application of a cheap, but sparingly soluble phosphate. The dry surface and subsoil contained respectively N = 0.1166 and 0.0969; P_2O_5 = 0.188 and 0.183; K_2O = 0.364 and 0.423; $CaCO_3$ = 3.139 and 2.239 per cent. Two plots of 100 square metres were manured as follows:—(1) No manure; (2) sodium nitrate, 200 kilos.; (3) same as (2), with soluble phosphoric acid, 50 kilos., as Spodium superphosphate (4) same as (2), with phosphoric acid, 500 kilos., as Redonda

phosphate. The crop was winter rye. The application of nitrate alone gave a very satisfactory increase, whilst phosphoric acid in both forms gave a still greater increase. The superphosphate gave rather more straw and less grain than the Redonda phosphate; but, on the whole, the effect of both manures may be considered equal.

N. H. J. M.

Pigeon Manure. By BERNHARD SCHULZE (*Bied. Centr.*, 1895, **24**, 590—591; from *Der Landwirt*, 1895, No. 51, 301).—The value of pigeon manure depends on the amount of water and sand which it contains, and on the very variable amounts of nitrogen, phosphoric acid, and potash. The following percentage results were obtained from 40 samples.

	Water.	N.	P ₂ O ₅ .	K ₂ O.
	3·80—40·00	1·47—5·04	1·00—2·77	0·71—2·57
Averages..	21·0	2·53	1·79	1·46

As much as 43·3 per cent. of sand was found.

N. H. J. M.

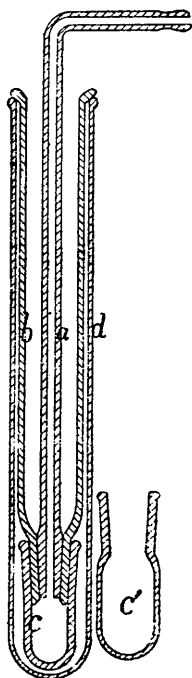
Analytical Chemistry.

New Method of Quantitative Spectrum Analysis. By GERHARD KRÜSS and H. KRÜSS (*Zeit. anorg. Chem.*, 1895, **10**, 31—43). —According to Lambert, if a ray of monochromatic light is passed through a layer of thickness m , and its luminosity is reduced $1/n$ th by a layer of unit thickness, the original luminosity J becomes $J' = J/n^m$. Assuming that the reduction in luminosity is the same for a layer of solution of thickness m and concentration c as for a layer of thickness c and concentration m , and that the luminosity is reduced $1/n$ th by a layer of thickness 1 and concentration 1, then $J' = J/n^{mc}$. Placing $n^{mc} = x$ we get $\log x = mc \log n$, or if $x = 10$, a condition that can be realised by so arranging the experiment that the luminosity of the light used is reduced to $1/10$ th of its original value by absorption in the solution,

$$c = \frac{1}{m \log n}.$$

It is evident that n is a constant for one and the same substance, and represents what may be termed the specific absorptive power of that substance. The constant k may be taken to represent the quantity $1/\log n$, and, therefore, $c = k/m$. If k has been determined by observation with a solution of known concentration, it will only be necessary to determine the thickness of the layer, m , of a similar solution of unknown concentration, required to reduce the luminosity to $1/10$ th of its original value, in order to find, c , the concentration. The authors describe a new spectrocoulometer with the aid of which a comparison of solutions of different concentration can be effected.

H. C.



Separation of Minerals of High Specific Gravity. By SAMUEL L. PENFIELD (*Amer. J. Sci.*, 1895, [3], 50, 446—448).—A description is given of a better form of apparatus than that previously described by Penfield and Kreider (*Abstr.*, 1894, ii, 456), to be used in the separation of minerals by aid of Retgers' double silver and thallium nitrate (*Abstr.*, 1893, ii, 294). The tube *b*, containing the heavy liquid and the material to be separated, fits into the cap *c*, and has its lower end closed by the stopper *a*; the whole is placed in a tube *d* in hot water. As the liquid is diluted, the successively lighter portions of the material are collected from the cap *c*. For dealing with large quantities of material, the larger cap *c'* is used. With larger amounts of thallium nitrate (than $\text{TlNO}_3 : \text{AgNO}_3 = 1 : 1$), the density and melting point increase until, for the pure salt, sp. gr. = 4.94 and m. p. = about 250° . As Retgers' liquid acts on mineral sulphides, it cannot be used for their separation. The specific gravity of the separated fragments is conveniently determined by weighing in water in a small tube suspended from the balance arm.

L. J. S.

New Reagent for Bromine and Iodine.

By J. H. KASTLE (*Amer. Chem. J.*, 1895, 17, 706—708).—Dichlorobenzenesulphonamide liberates bromine and iodine from metallic bromides and iodides, and can be used either in the solid state or in carbon bisulphide solution; it is recommended as a reagent instead of chlorine water, but, like this, excess must be avoided, otherwise iodine trichloride will be formed. It is possible to recognise the presence of iodine in solutions containing 0.0000127 and 0.00000635 gram, together with 0.04 and 0.00036 gram bromine respectively.

J. B. T.

Quantitative Separation of Bromine and Chlorine. By STEFAN BUGARSZKY (*Zeit. anorg. Chem.*, 1895, 10, 387—397).—The mixture of chloride and bromide is treated with from 50 to 100 c.c. of one-tenth normal potassium hydrogen iodate (according to the amount of bromine present), then with 10 c.c. of sulphuric acid (20 per cent. by volume), and the whole made up with water to 200 c.c. and boiled in a $\frac{1}{2}$ -litre flask until the volume is reduced to 60—80 c.c., whereby the liberated bromine and iodine are evolved. The residue in the flask is made up to 100 c.c. Half of this, diluted to 100 c.c., is treated with a little potassium iodide and titrated with $1/10$ th normal sodium thiosulphate. The amount of bromine is then calculated from the quantity of iodic acid used up by the oxidation.

The remaining half of the 100 c.c. is treated with sulphurous acid to reduce the iodic acid, the hydrogen iodide decomposed by sodium

nitrite, the solution then boiled until all the iodine is expelled, and the chlorine estimated by Volhard's method. The results are fairly accurate. Instead of determining the chlorine separately, the total amount of chlorine and bromine can be estimated by Volhard's method, and then the bromine estimated by the above method.

E. C. R.

Estimation of Sulphurous Anhydride and Sulphuric acid in the Products of Combustion of Coal Gas. By MAXIMILIANO DENNSTEDT and CÆSAR AHNENS (*Zeit. anal. Chem.*, 1896, **35**, 1—10).—The authors have repeated the work of Uno Collan (*Abstr.*, 1895, ii, 368), with the following modification. A flask of 11 litres capacity was fitted with a cork, through which passed three tubes. One of these, reaching to the bottom, was recurved and furnished with a jet for burning the gas; a second served for the admission of purified air; and the third was connected with a long Liebig's condenser sloping upwards. To the upper end of the condenser there was attached a Drehschmidt's absorption apparatus, with a Bunsen pump for aspirating a current of air through the whole system. It was assumed that the sulphuric acid formed would be retained in the flask and condenser, the sulphurous anhydride alone passing into the absorption apparatus. The results obtained were much more concordant than those of Collan, but the amount of sulphurous anhydride calculated from the chromic acid reduced was only (on the average) 80 per cent., whilst that found gravimetrically in the absorbing liquid was 92·5 per cent. of the whole. Seven flasks moistened with water, were then interposed between the condenser and the absorption apparatus. Sulphuric acid, to an average amount of 0·5 per cent., condensed in each of these flasks. The irregularities in the results seeming to be connected with variations in the air supply, the experiment was made of varying the relation of the sulphur to the oxygen by replacing the air by pure oxygen in one series of experiments, and in another increasing the sulphur by vaporising into the gas a known quantity of carbon bisulphide. With the oxygen atmosphere as much as 37 per cent. of the sulphur was directly burnt to sulphuric acid, whilst the addition of the carbon bisulphide caused an increase in the proportion escaping as sulphurous anhydride.

These facts are regarded as indicating that although sulphurous anhydride is the chief direct product of the combustion, it nevertheless, when diffused through an excess of atmospheric air, continues to oxidise until it is wholly converted into sulphuric acid. The injurious effects in rooms where coal gas is burnt are therefore in no way diminished by the fact that the sulphuric acid is formed at a distance from the flame, instead of in the flame itself.

M. J. S.

Estimation of Nitrogen in Peruvian Guano. By HEIBER (*Landw. Versuchs-Stat.*, 1895, **46**, 407—408).—The nitrogen in several samples of guano was determined by the Jodlbauer method, and by the washing out process. The guano was mixed with 2 parts of gypsum, and the acid (containing 40 grams of phenol per litre) added gradually, keeping well cooled; zinc dust was gradually added in small quantities. Loss of nitric oxide and of nitrophenol was thus

avoided. When all the zinc dust (3 grams) had been added, the whole was kept for a long time, after which 20 c.c. of strong sulphuric acid and mercury (2 grams) were added, and the decomposition proceeded with.

In the washing out method, the separation of the soluble and insoluble portions was carried out in the usual manner with 5 grams of guano. The filtrate was made up to 500 c.c., of which 100 c.c. was treated with caustic soda, iron dust, and zinc dust, and distilled after some hours.

The results, unlike those obtained by Haselhoff (Abstr., 1895, ii, 138), showed that the Jodlbauer method gave the higher percentages, owing probably to the fact that such compounds as guanine and uric acid are not decomposed by dilute soda. N. H. J. M.

Kjeldahl's Method and Platinochlorides. By W. VAN DAM (*Rec. Trav. Chim.*, 1895, 14, 217—226).—Délepine (Abstr., 1895, ii, 290) has shown that the percentage of nitrogen in certain platinochlorides, as estimated by Kjeldahl's method, falls considerably below the theoretical value. The author confirms this, and shows that by prolonging the heating and applying Gunning's modification of the method, the results are not improved. When Wilfarth's modification is employed (addition of a drop of mercury), the platinochlorides of several amines were found to yield satisfactory values for the percentage of nitrogen. Even under these circumstances, however, ammonium platinochloride yields low results. The last-mentioned compound gives theoretical values, as do the platinochlorides of all the amines tried, when a little zinc-dust is added to the concentrated sulphuric acid during the heating therewith.

Ethylamine aurochloride and ethylamine mercuriochloride give good results, both by Gunning's modification, and also by that of Wilfarth. The author has demonstrated that the whole of the nitrogen is evolved as such when ammonium platinochloride is heated with concentrated sulphuric acid for five hours. A. R. L.

Toxicological Estimation of Phosphorus. By PIETRO SPICA (*Chem. Centr.*, 1895, i, 562; from *Boll. Farm.*, 1895, 2).—After a portion of the material has been qualitatively tested by Mitscherlich's process, the remainder is treated as follows. It is put into a flask which is connected with a carbonic acid apparatus; the flask, after the air has been expelled, is gently heated on a sand bath, and the volatile products are passed through three Peligot tubes charged with a neutral solution of silver nitrate. To see whether all the phosphorus has passed over, the tubes are replaced by fresh ones; six to eight hours heating generally suffices to expel all the phosphorus.

The silver solution is oxidised, and, after precipitating the silver, the phosphoric acid is estimated by means of molybdate solution. The residue in the flask may still contain phosphorus in an incomplete state of oxidation, and capable of yielding hydrogen phosphide. Zinc is therefore added, and also dilute sulphuric acid a little at a time, so as to keep up a feeble current of hydrogen for about six days. All this time, a current of carbonic anhydride is also passed;

the gases are passed through Peligot tubes charged with silver nitrate solution, and should any precipitate form it is treated as before. L. DE K.

Testing for Arsenic in the Presence of Selenium. By L. DAWYDOW (*Chem. Centr.*, 1895, i, 811; from *Chem. Zeit. Rep.*, 19, 70).—The presence of selenium interferes with Marsh's test, and also with Bettendorf's stannous chloride test, and if present in large quantities, the first may fail altogether. The author recommends precipitating both arsenic and selenium by means of hydrogen sulphide, and then acting on the mixed sulphides with ammonium carbonate. The arsenical solution may then be further tested. L. DE K.

Decomposition of Silicates by Boric acid. By PAUL JANNASCH (*Ber.*, 1895, 28, 2822—2823).—Silicates may readily be brought into condition for analysis by fusion with boric acid. The boric acid is removed by repeatedly evaporating the solution with hydrochloric acid and methylic alcohol. A. H.

Estimation of Argon. By TH. SCHLOESING, jun. (*Compt. rend.*, 1895, 121, 525—528).—The author describes an arrangement of an ordinary mercury pump for passing a comparatively small, measured volume of nitrogen, containing argon, repeatedly through a tube containing heated magnesium. The last traces of argon are swept out of the tubes at the close of the operation by means of carbonic anhydride, and, before measuring the gas, any traces of nitrogen or of combustible gases are removed by sparking with oxygen in presence of potash, the excess of oxygen being afterwards absorbed by phosphorus (compare this vol., ii, 166). C. H. B.

Estimation of Calcium and Magnesium Carbonates in Soil. By ROBERT MAUZELIUS and ALBERT VESTERBERG (*Bied. Centr.*, 1895, 24, 583—584; from *Redogörelse f. verksamheten vid Ultuna Landtbruksinst. år, 1894. Upsala*, 1895, 62—71).—Extraction of calcium and magnesium carbonates with hydrochloric acid, and precipitation gives too high results. Carbonic anhydride was determined in 16 loamy soils (0.05 to 18.13 per cent. of CO_2) with a modified Fresenius' apparatus, and also the amount of lime and magnesia extracted by 0.9 to 1 per cent. hydrochloric acid. The carbonic anhydride represented by the lime and magnesia so determined, exceeded that actually found by 0.25 to 0.85 per cent. The results show that the amounts of readily decomposed zeolithic lime compounds in soils are too great to be neglected, especially in the case of soils poor in lime. In exact estimations, the carbonic anhydride should also be determined.

By increasing the strength of the acid to 4 per cent., much more lime and magnesia were dissolved. N. H. J. M.

Volumetric Estimation of Lead. By ALLERTON S. CUSHMAN and J. HAYES-CAMPBELL (*J. Amer. Chem. Soc.*, 1895, 17, 901—904).—Various methods for the volumetric estimation of lead have been

tried. A modified form of Schwartz-Diehle's method (Abstr., 1880, 752) is suggested. After the lead chromate has been filtered off, the excess of dichromate in solution is titrated by means of a standardised solution of ferrous ammonium sulphate, using potassium ferricyanide as an indicator, under exactly the same conditions as observed in standardising dichromate solutions. The results obtained are a trifle low. Low's method (*J. Anal. Chem.*, 6, 12) gave too high results. Knight's modification of Hempel's method (*ibid.*, 6, 11) did not yield concordant results.

J. J. S.

Electrolytic Separations. By EDGAR F. SMITH and DANIEL L. WALLACE (*J. Amer. Chem. Soc.*, 1895, 17, 612—615).—Mercury may be electrolytically separated from cadmium; gold from cobalt, arsenic, copper, zinc, and nickel; silver from zinc, nickel and cobalt, be operating at 65° in presence of potassium cyanide.

With a current of 0.02—0.08 ampère for mercury, 0.1 for gold, and 0.04 for silver, the deposition of the metal is generally complete in 3—3½ hours.

L. DE K.

Separation of Manganese from Zinc in Ammoniacal Solution by means of Hydrogen Peroxide under Pressure. By PAUL JANNASCH and E. VON CLOEDT (*Zeit. anorg. Chem.*, 1895, 10, 405—407).—A weighed quantity of manganese and zinc salts is dissolved in water (20 c.c.) and glacial acetic acid (10 c.c.), and poured into a cold mixture of 5 to 6 per cent. hydrogen peroxide (30 c.c.), concentrated ammonia (60 c.c.) and water (20 c.c.). The mixture is allowed to remain for 1½ hours in a thick walled glass flask closed with a rubber bung and capable of withstanding pressure, and is then heated for 1½ hours at the temperature of boiling water. The precipitated hydrated manganese dioxide is washed with ammonia and then with hot water; five to seven washings are usually sufficient to remove all traces of zinc. The filtrate containing the zinc is evaporated to dryness on the water bath, and then for a short time at 120—130° to remove the last trace of ammonium acetate. The residue is dissolved in water and dilute hydrochloric acid, and the zinc precipitated with sodium hydrogen carbonate.

E. C. R.

Separation of Iron from Beryllium. By ELIZABETH A. ATKINSON and EDGAR F. SMITH (*J. Amer. Chem. Soc.*, 1895, 17, 688—689).—The authors adopt the process introduced by von Knorre (Abstr., 1893, ii, 500) and separate the iron from beryllium by means of nitroso- β -naphthol. The iron solution containing about 0.1 gram of the metal is diluted to about 200 c.c. and 125 c.c. of a solution of the reagent in 50 per cent. acetic acid is added and the mixture is left for 24 hours. The iron precipitate is then collected and washed, first with 50 per cent. acetic acid and then with water until free from soluble matter. Owing to the slightly explosive nature of the compound, it is, after drying, mixed with an equal bulk of powdered oxalic acid and gradually heated until the carbon is burnt off, and the iron converted into oxide. The test-analyses show the accuracy of the process.

L. DE K.

Separation of Arsenic from Iron and Manganese. By PAUL JANNASCH and H. KAMMERER (*Zeit. anorg. Chem.*, 1895, 10, 408—414; see also Abstr., 1895, ii, 423).—*Separation of iron from arsenic.* Ammonium iron alum (0.5—0.6 gram), and arsenious anhydride (0.25—0.3 gram) are dissolved in 3 c.c. of a mixture of equal volumes of concentrated hydrochloric and nitric acids and a little water, and evaporated to dryness; the residue is dissolved in water and hydrogen peroxide, and poured into a mixture of sodium hydroxide (5 grams) water (50 c.c.) and hydrogen peroxide (30 c.c.). The mixture is heated to boiling, diluted to 250—300 c.c. and filtered. The iron precipitate is redissolved in dilute nitric acid and a little hydrogen peroxide, and again precipitated with ammoniacal hydrogen peroxide. The filtrates are evaporated in order to expel the ammonia, acidified with nitric acid, allowed to cool, and the arsenic precipitated with ammonia and magnesium chloride and weighed as $Mg_2As_2O_7$. *Manganese and arsenic* are separated in a similar way.

Separation of Iron from Nickel, Zinc, and Copper, in Hydrochloric acid Solution.—Ammonium iron alum, and nickel ammonium sulphate (0.5 gram of each) are dissolved in water (25 c.c.) and concentrated hydrochloric acid (6.7 c.c.), and poured into a mixture of ammonia, hydrogen peroxide, and water. The mixture is heated on the water bath, and the iron precipitate washed and redissolved in dilute hydrochloric acid containing hydrogen peroxide, and then again precipitated. The filtrates are evaporated to expel the ammonia, 1 gram of hydroxylamine added, and the nickel precipitated with excess of sodium hydroxide. The separation of iron from zinc, and iron from copper is carried out in a similar manner. The preceding separations are more easily effected when acetic acid is used instead of hydrochloric acid, since in the evaporation of the filtrates, the ammonium acetate is more easily volatilised. E. C. R.

Chromium Estimations. By JOHN E. STEAD (*Chem. Centr.*, 1895, i, 623—624; from *Journ. Iron and Steel Inst.*).—The author has improved Galbraith's process for the testing of chrome steel. The sample is dissolved in dilute sulphuric acid, filtered, the solution diluted to about 300 c.c., and heated to boiling. Strong solution of potassium permanganate is now added until the red colour is permanent for 10 minutes, then 80 c.c. of 10 per cent. hydrochloric acid, and the liquid heated until decolorised; 150 c.c. of water is added, about 100 c.c. boiled off to expel the chlorine, and the chromium is then titrated. The residue insoluble in dilute sulphuric acid is mixed with 0.5 gram of a mixture of 200 parts of calcium oxide, 50 parts of potassium carbonate and 50 parts of sodium carbonate and heated to intense redness for half an hour; the chromium is afterwards titrated in hydrochloric acid solution with ferrous sulphate and potassium dichromate.

Another process consists in dissolving 2 grams of the sample in hydrochloric acid; without filtering, the liquid is nearly neutralised with a 2 per cent. solution of sodium hydroxide, and after diluting to 300 c.c., 10 c.c. of a 5 per cent. solution of disodium hydrogen phosphate and 30 grams of sodium thiosulphate is added. After

boiling to expel the sulphurous acid, 20 c.c. of a saturated solution of sodium acetate is added and the boiling continued for 5 minutes; the precipitated chromium phosphate is then washed with a 2 per cent. solution of ammonium nitrate, dried, calcined, and fused with the above lime mixture. The melt, dissolved in 30 c.c. of hydrochloric acid and 150 c.c. of water, is boiled for 10 minutes and titrated. The process may be used in presence of vanadium. In this case, the chromium must be titrated by means of ferrous sulphate and potassium permanganate in presence of sulphuric acid.

L. DE K.

Separation of Chromium from Manganese, Iron, and Aluminium. By PAUL JANNASCH and E. VON CLOEDT (*Zeit. anorg. Chem.*, 1895, 10, 398—404).—*Separation of Manganese and Chromium.*—Manganese ammonium sulphate and ammonium chrome-alum (0.35—0.4 gram) are dissolved in water (50 c.c.) and concentrated nitric acid (5 c.c.), and the solution poured into a mixture of 3 per cent. hydrogen peroxide (40 c.c.) and soda (1 : 5, 40 c.c.). The mixture is heated to boiling, and the precipitate of hydrated manganese dioxide washed with dilute ammonia containing hydrogen peroxide, is dissolved in nitric acid containing hydrogen peroxide, and again subjected to the above method of precipitation. The precipitate, which contains traces of soda, is redissolved and precipitated with ammoniacal hydrogen peroxide, then dried, and heated to a constant weight. The filtrates, which contain the chromium as sodium chromate, are concentrated and treated with hydrochloric acid and alcohol, whereby the chromate is converted into chromium chloride; and the solution, freed from alcohol, is diluted, treated with hydroxylamine chloride (0.5 gram) and carefully precipitated with ammonia.

Manganese and chromium are more readily separated by treating their mixed salts under pressure with ammoniacal hydrogen peroxide, whereby only one precipitation is necessary. The solution of the salts mixed with 6 per cent. hydrogen peroxide (80 c.c.) and concentrated ammonia (30 c.c.) is allowed to remain a short time in a thick-walled glass flask closed with an india-rubber stopper, and is heated for 1—2 hours at the temperature of boiling water; the flask is then opened, and the precipitate washed and treated as previously described. It is most essential to use 6 per cent. hydrogen peroxide, as, if weaker solutions are employed, the precipitate contains chromium. *Iron and chromium* are easily separated in the same way.

Aluminium and chromium are separated in a similar way, but pressure is not necessary. 5—6 per cent. hydrogen peroxide is used, and after the mixture has been allowed to remain 1—2 hours in the cold, it is heated until all but the last traces of ammonia are removed. The precipitate of aluminium hydroxide must be washed with great care.

E. C. R.

Warning against the Use of Fluoriferous Hydrogen Peroxide in Estimating Titanium. By WILLIAM F. HILLEBRAND (*J. Amer. Chem. Soc.*, 1895, 17, 718—719).—In estimating titanic acid coloro-

metrically, the hydrogen peroxide employed must be free from fluorine compounds, as even a minute amount will weaken the yellow coloration, or even entirely prevent its formation. L. DE K.

Electrolytic Estimation of Ruthenium. By EDGAR F. SMITH and HARRY B. HARRIS (*J. Amer. Chem. Soc.*, 1895, **17**, 652—654).—The authors have found that ruthenium may be conveniently deposited by electrolysis best in presence of acid sodium phosphate. Sodium acetate may also be used, but the deposit is then inclined to be spongy.

The platinum dish in which the decomposition is carried out must be coated inside with copper. If the amount of ruthenium does not much exceed 0.05 gram, a current of 0.01—0.05 ampère acting for about six hours will suffice. Ruthenium may be thus separated from iridium. L. DE K.

Testing Ethereal Oils. By EDUARD HIRSCHSOHN (*Chem. Centr.*, 1895, i, 695—696; from *Pharm. Zeit. Russ.*, **34**, 97—102, 113—119).—Two kinds of oil of thyme exist; when distilling samples of the first group, the first two distillates measure over 70 per cent., of which nearly 13 per cent. is soluble in 2—4 vols. of 70 per cent. alcohol, whilst the second group yields 62 per cent. of the first two distillates, 12—31 per cent. of which is soluble. The different fractions give different colour reactions, showing that the commercial oils vary in constitution.

Oil of patchouli should dissolve in an equal bulk of 90 per cent alcohol; if not, adulteration with copaiba may be suspected.

Oils of rosemary of French, Italian, and Spanish origin all give the iodol reaction. When distilling the French samples, the first two fractions amounted to 62—68 per cent., and the last fractions to 20—27 per cent.; the first fraction is soluble in 3 vols. of 90 per cent. alcohol, and the last fractions give, with bromoform and acetic acid, a strong reaction. Of Italian samples, the first distillate amounts to 46 per cent. soluble in 10 vols. of 80 per cent. alcohol; the first two distillates amount to 78 per cent. The first distillates of the Spanish oils are more soluble in 80 or 70 per cent. alcohol. L. DE K.

Estimation of Simple Cyanides in the Presence of Compound Cyanides and certain other Substances. By J. E. CLENELL (*Chem. News*, 1895, **72**, 227—229).—The iodine method is not seriously interfered with by ferrocyanides, ferricyanides, or thiocyanates, but with the silver nitrate method the first salts render the results somewhat too high; the second salts have the reverse effect, and the third salts render the end reaction obscure. In the presence of zinc, neither method is trustworthy, so that the total cyanide and zinc must then be determined. The zinc is determined by adding a known excess of standard ferrocyanide, acidifying and titrating the unexhausted residue with permanganate; in the absence of substances which react with iodine, the total cyanide may be estimated in neutral or neutralised solutions containing both simple cyanides.

and zinc double cyanide by adding excess of ferrocyanide, and titrating with standard iodine. D. A. L.

Technical Analysis of Cyanide Working Solutions. By WILLIAM BETTEL (*Chem. News*, 1895, **72**, 286—287).—The methods apply to the McArthur-Forrest working solutions containing zinc. Free cyanide is estimated by titrating 50 c.c. with silver nitrate to faint opalescence or precipitate; this will indicate (if sufficient ferrocyanide is present to form a flocculent precipitate of zinc ferrocyanide) the free cyanide and cyanide equal to 7.9 per cent. of the potassium zinc cyanide present. Hydrocyanic acid is estimated in 50 c.c. by adding sodium or potassium hydrogen carbonate and titrating as for free cyanide. Double cyanides are estimated by adding excess of caustic soda to 50 c.c. of the solution, then a few drops of 10 per cent. potassium iodide, and titrating with silver nitrate to opalescence. On deducting the free cyanide and hydrocyanic numbers, the result is potassium cyanide due to double cyanide, the quantity of which may be obtained by multiplying by 0.9493 and adding 7.9 for every 92.1 parts of potassium zinc cyanide indicated. D. A. L.

Estimation of Rosin Oil in Mineral Oil. By J. KLIMONT (*Chem. Centr.*, 1895, i, 563; from *Chem. Rev. Fett Harz-Ind.*, 1895, **10**, 4—5).—The author applies his bromine process (*Abstr.*, 1895, ii, 91). Rosin oils give an average turpentine number (*loc. cit.*) of 51; mineral lubricating oils of only about five. The amount of rosin oil may, therefore, be estimated by the aid of the equations $51x/100 + 5y/100 = a$ and $x + y = 100$, in which a represents the turpentine number of the sample, x the percentage of rosin oil, and y the amount of mineral oil. L. DE K.

Estimation of Total Solids and Alcohol in Wine by an Optical Method. By E. RIEGLER (*Zeit. anal. Chem.*, 1896, **35**, 27—31).—The refractive index of a wine may be regarded as consisting of three parts— a , that due to the water; b , that due to the solids; c , that due to the alcohol. The presence of each gram of alcohol in 100 c.c. of the wine causes an increase of 0.00068 in the index of refraction. In the wine freed from alcohol, each gram of solids raises the index by 0.00145 (extremes observed are 0.00137 and 0.00150). A quantity of the wine (25 c.c.), measured in a flask, is evaporated on the water bath to about 8 c.c., returned to the flask, and made up with distilled water to the original volume. The refractive index ($a + b$) of the resulting solution, that of the original wine (N), and that of distilled water (a) are then determined after the three liquids have been brought to exactly the same temperature by plunging them into a vessel of water of the temperature of the workroom. Pulfrich's refractometer (*Zeit. anal. Chem.*, **28**, 81) gives results to the 5th decimal place with ease and rapidity. Then $\frac{N - (a + b)}{0.00068}$ gives grams of alcohol, and $\frac{(a + b) - a}{0.00145}$ grams of solids per 100 c.c. of wine. From the exami-

nation of a single sample of beer, the constants seem to be the same for beer as for wine. M. J. S.

The Cyano-cupric Estimation of Glucose. By ALFRED W. GERRARD (*Pharm. J. Trans.*, 1895, [3], 25, 913).—The author has improved the formula for his cyano-cupric test for glucose, and now adopts the following. To 10 c.c. of Fehling's solution, heated to boiling in a porcelain dish, a 5 per cent. solution of potassium cyanide is gradually added until only a very faint blue colour remains. Another 10 c.c. of Fehling's solution is now added, and while the mixture is kept boiling, the solution of sugar or urine is run in slowly from a burette until the blue colour disappears. The volume of liquid required will contain 0.05 gram of glucose. R. R.

Analysis of Urine. Estimation of small Quantities of Sugar by means of Nylander's Bismuth Solution. By GEORG BUCHNER (*Chem. Centr.*, 1895, i, 303; from *Münch. med. Wochschr.*, 41, 991).—The bismuth solution should be added to the urine in the proportion of 1—10. Ammonium carbonate in large quantity, albumin, rhubarb, senna, salol, antipyrine, turpentine, or other drugs likely to yield compounds with glycuronic acid, must be absent. The test will distinctly show the presence of 0.025 per cent. of sugar by the grey colour of the phosphatic precipitate. The author has, however, noticed urines which give this reaction, although, when examined by the phenylhydrazine test, they were found to contain no sugar. The reaction with the bismuth was here probably caused by the presence of uroerythrin which occurs in abnormal quantity in the urine of persons suffering from fever, rheumatism, liver complaints, or diarrhoea, and also often contains an increased amount of uric acid, creatinine, and colouring matters. The greyish colour of the phosphatic precipitate can only be taken as an indication of the presence of sugar when a pure white deposit is obtained after boiling with aqueous potash. L. DE K.

Estimation of Sugar in Preserved Fruits. By JOS. MAYRHOFER (*Chem. Centr.*, 1895, i, 898—899; from *Forsch.-Ber. Lebensm. u. Hyg.*, 1895, 75—79).—The author states that the official method for the detection of glucose in jams is not trustworthy, and proposes a modification. The sugar mixture is inverted and titrated with Fehling's solution, and the result calculated as cane sugar, from which the polarisation is then calculated. If glucose is present, the calculated polarisation will be more than the observed, and 5 per cent. of this substance may thus be detected. L. DE K.

Estimation of Cane Sugar in Malt. By ED. JALOWETZ (*Chem. Centr.*, 1895, i, 934; from *Zeit. angew. Chem.*, 1895, 208—209).—The actual polarisation of the solution is first observed in the 20-cm. tube of Laurent's apparatus; 75 c.c. is then heated with 5 c.c. of hydrochloric acid (sp. gr. 1.88) in a narrow necked 100 c.c. flask at 69—71° for 10 minutes. After inversion, 1 gram of animal charcoal is added, the liquid cooled to 20°, then made up to the mark, and

filtered. The filtrate is again polarised, and due allowance made for dilution. The amount of cane sugar in 100 c.c. of malt infusion is found by dividing the difference in the two polarisations by 1.782.

L. DE K.

Estimation of Formaldehyde. By M. KLAR (*Zeit. anal. Chem.*, 1896, **35**, 116—117; from *Pharm. Zeit.*, **40**, 611).—Formaldehyde may be estimated by treatment with an aqueous solution of aniline, when methyleneaniline, $C_6H_5 \cdot N \cdot CH_2$, is precipitated, and may be collected, dried at 40° , and weighed. A more expeditious method consists in titrating the excess of aniline in the filtrate, using Congo-red as indicator. For such a formaldehyde solution as that of the German Pharmacopœia, 400 c.c. of aniline solution (3 grams of aniline per litre) is placed in a flask, and 1 c.c. of the formaldehyde solution added by drops with shaking. The mixture is made up to 500 c.c., and, after some time, filtered. The excess of aniline is then estimated in 50 c.c., taking as the end point that at which the red colour acquires a strong, bluish tone, remaining unaltered on the further addition of a small quantity of acid. The original aniline solution is similarly titrated. One c.c. of N/10 acid corresponds with 0.003 gram of formaldehyde.

M. J. S.

Estimation of Benzoyl and Acetyl Groups. By RICHARD MEYER and HEINRICH MEYER (*Ber.*, 1895, **28**, 2965—2969).—About 0.5 gram of the substance is placed in a round-bottomed flask of 250 c.c. capacity, 30—50 c.c. of alcohol is added, and then caustic potash in excess, the whole being heated in a reflux apparatus until the hydrolysis is complete. The contents of the flask are then acidified with a strong solution of phosphoric acid, and distilled with steam; after $1-1\frac{1}{2}$ litre has passed over, each successive 150 c.c. or so of the distillate is titrated until it is found to contain no more acid. The bulk of the distillate is meanwhile treated with a drop of rosolic acid and a measured excess of N/10 soda, rapidly concentrated in a platinum, silver, or nickel dish over a spirit burner to a volume of 100—150 c.c., and the excess of alkali determined by titration with N/10 acid in boiling solution. The results obtained are a little high, 0.5—1.0 c.c. more alkali being used than is theoretically necessary, owing to the absorption of acid during evaporation. The caustic potash and phosphoric acid used must not contain either nitrous or nitric acid; a little potassium chloride in the potash does not matter when phosphoric acid is used, but it would be prejudicial were sulphuric acid used instead, as hydrochloric acid would then be set free from it.

The above applies to the estimation of benzoyl groups. Acetyl groups can be estimated in the same way, but more easily; the distillation, which can be stopped when the distillate is no longer acid to litmus paper, does not take so long; phenolphthaleïn should be used as an indicator in the titration.

C. F. B.

Separation of Solid and Liquid Fatty acids. By LEONARD DE KONINGH (*J. Amer. Chem. Soc.*, 1895, **17**, 740—741).—Twitchell (*ibid.*, 290) has attempted to show that Muter's process for the separa-

tion of solid and liquid fatty acids is erroneous on account of the slight solubility of the lead salts of the solid fatty acids in ether and their probable greater solubility in ether containing lead oleate. The iodine figure of the liquid acids is also said to be erroneous, chiefly on account of a supposed oxidation which occurs when applying this method. The author thinks that, when present in fair proportion, the separation of the liquid from the solid fatty acids by the lead ether method is fairly complete; the iodine figures of the isolated fatty acids are also trustworthy, and the danger of oxidation is greatly exaggerated.

L. DE K.

Estimation of Uric acid by Fehling's Solution. By E. RIEGLER (*Zeit. anal. Chem.*, 1896, **35**, 31—34).—An alkaline solution of uric acid boiled with Fehling's solution throws down cuprous oxide, the average amount of copper in the precipitate being 0.8 gram for 1 gram of uric acid. The extreme values in 10 experiments were 0.7812 and 0.8333 gram. To estimate uric acid in urine, it is first separated in the form of ammonium urate as follows. 200 c.c. of urine is mixed with 10 c.c. of a saturated solution of sodium carbonate, and after half an hour, the precipitate of phosphates is filtered off, and washed with about 50 c.c. of hot water. The filtrate, mixed with 20 c.c. of a saturated solution of ammonium chloride, is stirred well, and left for five hours. The precipitate is then collected on a small filter, washed with 50 c.c. of water, and then rinsed through the pierced filter with 50 c.c. of water into a 300 c.c. beaker; 60 c.c. of Fehling's solution (30 c.c. of copper sulphate solution containing 69.2 grams of the crystallised salt per litre, and 30 c.c. of alkaline tartrate solution containing 346 grams of sodium potassium tartrate, and 250 grams of potassium hydroxide per litre) is added, and the mixture boiled gently for five minutes. After thorough subsidence, the liquid is filtered through a small (9 cm.) close filter, and the precipitate thoroughly washed with hot water. It is then dissolved from the filter by 20 c.c. of hot nitric acid of 1.1 sp. gr., and the filter washed with about 60 c.c. of water. The solution is neutralised with powdered dry sodium carbonate, until a slight turbidity is produced; the turbidity is cleared up with a few drops of dilute sulphuric acid, and the whole made up to 100 c.c. 25 c.c. of the liquid is then mixed with 1 gram of potassium iodide, and after 10 minutes, starch paste is added; the liberated iodine is then titrated by thiosulphate solution, made by diluting 126 c.c. of N/10 solution to 500 c.c. 1 c.c. of this solution corresponds with 0.002 gram of uric acid.

M. J. S.

Detection of Salicylic acid in Beer. By R. J. L. SCHOEPP (*Ned. Tydschr. Pharm., &c.*, **7**, 67—71).—The process generally employed is to agitate the acidified sample with a mixture of 2 parts of ether and 1 part of light petroleum, as ether alone also dissolves colouring matters. The author found, however, that when applying the well known ferric chloride test, the salicylic acid reaction was occasionally obtained with samples which were undoubtedly free from adulteration, this reaction being due to maltol, a substance recently isolated by Brand (*Abstr.*, 1894, i, 270) from roasted malt. Maltol

does not, however, give any particular reaction with Millon's reagent, whereas salicylic acid gives a dark red coloration. In beer analysis, this test should be employed, as well as the ferric chloride test.

L. DE K.

Examination of Oil of Bergamot. By ARTHUR BORNTÄGER (*Zeit. anal. Chem.*, 1896, **35**, 35—38).—The proportion in bergamot oil of the linalol acetate, which is its essential odoriferous constituent (Abstr., 1892, 868), being fairly constant, namely, 34—43 per cent. according to Schimmel and Co., 37.6—39.9 per cent. according to the author, an estimation of its amount by saponification serves to detect the presence of oil of turpentine, the most usual adulterant of bergamot oil. About 2 grams of the oil is cohobated for 1—2 hours with 20 c.c. of N/2 alcoholic potash, and titrated back with N/2 sulphuric acid and phenolphthaleïn.

The oil evaporated on the water-bath should not leave more than 6 per cent. of residue. This residue contains 1—2 per cent. of saponifiable substances, the amount of which should be deducted when estimating the linalol acetate. A large percentage of non-volatile saponifiable substance would point to the addition of a fatty oil. Colophony would be indicated by a high residue containing free acids (abietic, &c.), the genuine oil containing only traces either of colophony or of free acid.

M. J. S.

Estimation of Fat in Milk. By H. WELLER (*Chem. Centr.*, 1895, i, 898; from *Forsch. Ber. üb. Lebensm.*, 1895, 80—83).—10 c.c. of the sample is poured into a weighed cylindrical aluminium tube containing about 3 grams of cotton wool, previously extracted with ether. The exact quantity of milk is found by reweighing the tube.

After drying in a special drying apparatus, the total solids are obtained. After extracting the fat in a suitable extractor, the residue is again dried and reweighed. The loss represents the fat, but after evaporating the ether, the fat may be also directly weighed.

L. DE K.

Rapid Estimation of Fats in Milk: a new Lactobutyrometer By ANTONIO LONGI (*Gazzetta*, 1895, **25**, i, 441—451).—The author describes and sketches a new simple form of lactobutyrometer, which he has used with excellent results for some years past.

W. J. P.

Examination of Lard for Impurities. By DAVID WESSON (*J. Amer. Chem. Soc.*, 1895, **17**, 723—735).—The author has investigated most of the published physical and chemical methods for the analysis of lard, and concludes that, unless the origin of the sample is known, no method gives satisfactory results, particularly if the amount of adulteration is small.

If cotton-seed oil is suspected, the only trustworthy test is the one based on the iodine absorption of the liquid fatty acids, but it must be remembered that American lard differs greatly from the European article, and has a much higher iodine absorption.

L. DE K.

General and Physical Chemistry.

The Atomic Refraction of Oxygen. By FRANCESCO ANDERLINI (*Gazzetta*, 1895, 25, ii, 127—162).—The author has determined the refraction equivalents of a number of oxygen compounds of different types, for the hydrogen lines α , β , and γ , and gives the refraction and dispersion constants; the results for the ray H_{α} are summarised in the appended table. The methods of preparation and the criteria of purity of the several substances are given.

	<i>t.</i>	$P \frac{\mu_{H_{\alpha}} - 1}{d}$		$P \frac{\mu^2_{H_{\alpha}} - 1}{(\mu^2_{H_{\alpha}} + 2)d}$	
		Observed.	Calculated.	Observed.	Calculated.
Dipropionyl	26·3°	101·53	100·8	60·28	60·18
"	5·6	101·78	100·8	60·78	60·18
Dibutylryl	20·0	133·2	131·2	79·76	78·42
Isodivaleryl	24·5	163·28	161·6	97·70	96·66
"	6·2	162·9	161·6	97·49	96·66
γ -Valerolactone	22·4	41·03	41·6	24·64	21·64
"	16·9	40·97	41·6	24·59	21·64
γ -Isocapro lactone	16·2	48·6	49·2	29·18	29·20
"	14·9	48·55	49·2	29·14	29·20
Pyrotartaric anhydride...	13·7	41·54	42·4	24·81	24·90
Propionic anhydride...	23·3	51·80	52·6	31·39	31·54
"	23·9	51·82	52·6	31·41	31·54
Isovaleric anhydride...	26·7	82·66	83·0	49·85	49·78
"	23·2	82·57	83·0	49·98	49·78
Propoïn	16·6	52·59	51·8	31·62	31·28
Butyroïn	16·7	68·4	67·0	41·06	40·4
Isovaleroïn	17·4	82·8	82·2	49·6	49·52
Diphenylmethane	16·8	95·21	95·0	54·92	55·28
Succinic anhydride	20·4	34·10	34·8	20·37	20·35
Maleïc anhydride	19·20	33·09	34·6	20·28	20·04
Lactide	9·9	51·86	52·8	31·10	31·04
"	20·8	52·12	52·8	31·69	31·04
Benzoic anhydride.....	14·9	109·23	107·0	63·04	62·06
Benzile	13·0	108·14	104·2	63·40	60·48
"	7·0	107·55	104·2	63·56	60·48
Coumarin	7·3	73·0	68·6	43·18	39·70
"	7·7	73·0	68·6	42·91	39·70
Phenolphthaleïn	5·5	159·4	151·6	91·82	87·26
Dimethylfumaric anhy- dride	19·4	51·0	49·8	30·83	29·16
Terebic acid	24·4	58·0	58·4	35·8	35·50
Triphenylmethane.....	18·4	138·1	137·4	81·37	79·78

Maleïc, dimethylfumaric, and benzoic anhydrides, benzile, coumarin, and triphenylmethane were examined in benzene, lactide and terebic acid in acetone, succinic anhydride in acetic acid, and phenolphthaleïn

in alcoholic solution; the other substances mentioned in the table were examined in the pure liquid state. Dipropionyl, dibutyryl, and isodivaleryl have been shown to be really diethylacetylenic dipropionate, dipropylacetylenic dibutyrate, and diisobutylacetylenic diisovalerate respectively (Klinger and Schmitz, *Abstr.*, 1891, 890; Anderlini, this vol., i, 202); the molecular refractions are therefore calculated in accordance with these facts.

The difference between the observed and calculated values of the molecular refraction are usually too great to be ascribed to experimental error, showing that the refraction constants are intimately affected by small changes in constitution, which cannot yet be accurately valued owing to the lack of experimental data.

W. J. P.

Modified form of Polarimeter for Chemical Purposes. By HANS HEINRICH LANDOLT (*Ber.*, 1896, 28, 3102—3104).—The author describes a form of apparatus which facilitates the examination of rotatory liquids at temperatures extending over a wide range, the substance being introduced into a brass tube enclosed in a jacket constructed of sheet brass; a vertical, tubular limb of small bore allows for the contraction or expansion of the contents of the brass tube, the inner surface of which is gilded. Moreover, a simple lever replaces the micrometer screw for the purpose of controlling the analyser, and, by employing a Lippich polariser, the length of the instrument is reduced, owing to the fact that a 2-decimeter tube is sufficiently long for most purposes, consequent on the accuracy with which the neutral tint may be observed.

M. O. F.

Cause of Birotation. By EDMUND O. VON LIPPMANN (*Ber.*, 1896, 29, 203—204).—The author, in his book, *Chemie der Zuckerarten*, suggested stereochemical changes as the cause of birotation before either Lobry de Bruyn and van Ekenstein (this vol., i, 116), or Trey (*ibid.*, ii, 139).

C. F. B.

Loss of Energy of a Battery during Electrolysis. By HANS JAHN (*Zeit. physikal. Chem.*, 1895, 18, 399—425).—By the direct measurement of the heat developed in the battery, and the calculation of that developed in the circuit, the author obtains the total heat development per unit current, (I) without, (II) with, polarisation. The difference is the energy necessary for the decomposition of the corresponding quantity of the electrolyte, from which that necessary for the decomposition of the milligram equivalent is obtained, and the value of the polarisation is deduced. The last two values are given (for 0°) in the accompanying table, under the headings *w* and *p*, dp/dt being the heat coefficient (in volts) of the polarisation between 0° and 40°, at which temperatures the experiments were performed.

The values for the polarisation are, in all cases, markedly higher than those obtained by other methods. The difference between the heat value thus obtained and the heat of formation of the electrolyte must equal the heat produced in the decomposition cell. Owing to the Peltier effect, the quantities of heat produced at the two electrodes differ, and from the differences actually obtained the Peltier

	<i>w.</i>	<i>p.</i>	$dp'/dt.$
Copper sulphate	79·86	1·756	-0·00508
Zinc sulphate.....	126·88	2·790	-0·00524
Cadmium sulphate	111·15	2·444	-0·00315
Copper nitrate.....	81·31	1·788	-0·00465
Lead nitrate*	—	2·267	-0·00460
Silver nitrate*	—	1·330	-0·00382

effect is determined, in the case of copper | copper sulphate, zinc | zinc sulphate and cadmium | cadmium sulphate junctions, the values so derived agreeing satisfactorily with those calculated from the thermo-electromotive forces of the junctions. Next is calculated the cathodic, and hence the anodic polarisation, the values for the latter being somewhat greater for sulphates than for nitrates. The heat of ionisation of the metal is also readily obtained, and the values agree well, as would be expected, with the heats of solution of the metals in dilute nitric or hydrochloric acid.

L. M. J.

Electrical Conductivity of Salts dissolved in Glycerol. By CARLO CATTANEO (*Real. Accad. Lincei*, 1893, ii, 112—119).—In continuation of his work on the electrical conductivity of salts dissolved in water, alcohol, and ether (*Real. Accad. Torino*, 1893), the author has determined the conductivities of solutions of ammonium, sodium, zinc, barium, and ferric chlorides, and potassium bromide and iodide, in glycerol containing 2·5 per cent. of water, at various temperatures between 0° and 24°.

The conductivity of the various salts is, in general, greater than that of the corresponding ethereal solutions, but less than that of the alcoholic ones; the conductivity of the aqueous, alcoholic, and glycerol solutions increases more slowly than the concentration, but that of the ethereal solutions increases more rapidly than the concentration. As the concentration decreases, the molecular conductivity of the salts in aqueous solution increases, and in ethereal solution decreases; that of the chlorides increases, whilst that of the bromides and iodides decreases, in alcoholic solution, and in glycerol, the molecular conductivity of the chlorides increases whilst the concentration decreases. The temperature coefficients are usually greater for aqueous than for alcoholic solutions; in ether, they are of approximately the same order as in water, but are negative in sign, whilst, in glycerol, the temperature coefficients have very high values.

A table of the conductivities of the glycerol used at various temperatures is given, showing that it obeys the rule enunciated by Bartoli, which states that those carbon compounds which become most viscous on cooling are those whose conductivity increases most rapidly as the temperature rises. At 18°, the conductivity of the glycerol was found to be of the order of 10^{-12} .

W. J. P.

* These values are calculated from those of copper nitrate by aid of the known E.M.F. of Cu—Ag and Cu—Pb cells.

Absorption of Acid and Alkali from Solutions by Platinum Black. By CARL KELLNER (*Ann. Phys. Chem.*, 1895, [2], 57, 79—90).—Kohlrausch observed that the conductivity of solutions of certain acids and bases decreases slowly when determined in vessels containing platinised electrodes, and that, if the solution is removed from the vessels, the electrodes washed several times with distilled water, and the conductivity then redetermined, it will be found to have returned to its original value. Neutral salt solutions do not exhibit this behaviour. The author has examined solutions of a number of acids and bases, and finds that the peculiarity here spoken of is due to an absorption of some of the acid or alkali by the platinum black of the platinised electrodes. The acid or alkali absorbed is given up again to distilled water, as is shown by the gradual rise in the conductivity of water placed in the resistance vessels after the acid or alkali has been removed. It is only in this way that the absorption by the electrodes can be determined, as the absolute quantities absorbed are too minute to be detected by the ordinary chemical tests. H. C.

Production of very Low Temperatures and Liquefaction of Gases. By C. LINDE (*Ann. Phys. Chem.*, 1895, [2], 57, 328—332).—The gas at the temperature t_1 is brought in the compressor from the pressure p_1 to the pressure p_2 , and then, after cooling by a water jacket, passes into the inner tube of the cooling apparatus, from which it issues through a throstle valve, the temperature undergoing, on expansion of the gas, a reduction of t_2 — t_3 . In the cooling apparatus, it has met, at the temperature t_3 , with the reverse current of expanded gas passing through the outer tube of the apparatus. Temperature equilibrium is here established, and the gas, after traversing the outer tube of the cooling apparatus, returns to the compressor again with the pressure p_1 and temperature t_5 . In this way, by successive compressions and expansions, the gas may be cooled until, on expansion, it partly liquefies, and with an apparatus of this kind liquid air has been obtained.

The author claims that the apparatus recently described by Dewar for liquefying air, is identical with the above (compare, however, Dewar, *Proc.*, 1895, 221). H. C.

Dependence of the Specific Heat of Water on the Temperature. By KONRAD DIETERICI (*Ann. Phys. Chem.*, 1895, [2], 57, 333—338).—If two quantities of water at different temperatures are mixed, and C_{hm} is the mean specific heat of water between the higher temperature and that of the mixture, and C_{nm} the mean specific heat between the lower temperature and that of the mixture, then

$$C_{hm} = aC_{nm}.$$

The specific heat has here no simple physical meaning, but is made up of the specific heat c at constant volume and the heat of expansion δ , and the equation may, therefore, be given in the form

$$c_{hm} + \delta_{hm} = a(c_{nm} + \delta_{nm}).$$

From the experiments of Baumgartner-Pfaundler, Münchhausen-Wüllner, Velten, and Lüdin, the author has calculated the specific

heat at constant volume c as a function of the temperature, and so obtained the equation

$$c_t = c_0(1 - \alpha t - \beta t^2),$$

in which $\alpha = 0.00062$, $\beta = 0.0000042$, and $c_0 = 0.9996$. The specific heat of water at constant pressure and at 0° is taken as unity. From the above it will be seen that the specific heat at constant volume decreases with rising temperature; δ , on the other hand, increases with the temperature, and the sum of the two quantities which gives the specific heat at constant pressure first decreases and then rises with increasing temperature. H. C.

The Thermal Expansion of Salt Solutions. By S. DE LANNON (*Zeit. physikal. Chem.*, 1895, **18**, 442—472).—The dilatometric method is employed in preference to other methods, reasons for its adoption being given. The various corrections applied to the results are stated, and the possible error of the determinations estimated as 0.000088. This is probably of the order of the actual probable error, for, although above the mean value in the experimental work, it is apparently not unfrequently reached. The thermometers employed were compared with an air thermometer, and the various corrections for the exterior cooled portion of the tube, the alterations of the zero-point, &c., are applied to the readings. The dilatometers are stated to have been calibrated, but no mention is made of the method of calibration employed. The experimental observations are reproduced by the unsatisfactory method of two expansion formulæ of the form $1 + \alpha t + \beta t^2$, the one available below, the other above 40° , but in some cases one formula suffices for the complete range. The observed results and those given by the expansion formulæ appear to agree satisfactorily, but are not compared in the paper, where comparisons are given only between the calculated values and those obtained from curves. The solutions examined were those of ammonium nitrate, potassium ferrocyanide, potassium bromide, ammonium sulphate, zinc sulphate, sodium nitrate, lead nitrate, strontium nitrate, and magnesium sulphate at various concentrations, and complete tables are given showing the composition of the solution, the expansions observed, the expansion formulæ, density, and temperature of maximum density which, however, most probably has no real significance. The author postpones the discussion of the results. L. M. J.

Normal Boiling Tube. By GEORG W. A. KAHLBAUM (*Ber.*, 1896, **29**, 71—73).—The boiling column described by the author consists of an outer tube, which is fitted into the distilling vessel, and an inner tube, which communicates at its lower extremity with the condenser. The thermometer, which is placed in the inner tube, is thus surrounded by a double envelope of vapour, and is also screened from projected particles of liquid. M. O. F.

Boiling Point and the Genesis of the Elements. By CHARLES T. BLANSHARD (*Chem. News*, 1895, **72**, 299—301).—The differences in the boiling points of elements in various groups are compared with

the differences in boiling points in various homologous series of carbon compounds. From the results, the author concludes that the elements of groups I to IV are less highly evolved than the other elements.

D. A. I.

Phenomena observed at the Critical Point. By GIULIO ZAMBIASI (*Real. Accad. Lincei*, 1892, ii, 423—431).—The gaseous and liquid forms of a substance are supposed to have the same specific volumes at the critical temperature; this assumption was made by van der Waals in dealing with the continuity of the liquid and gaseous states. Cailletet found, however, that in the case of carbonic anhydride, the meniscus disappeared before the specific volumes of the liquid and gas became quite equal. The author has investigated the critical point of ether in the following manner. Ether is sealed in an annular tube containing mercury, in such a way that the mercury in the two arms is surmounted by unequal heights of ether; on very gradually and regularly raising the temperature of the tube to the critical temperature of ether, the mercury in the two arms of the tube should attain the same level at the instant the meniscus disappears. This, however, is not the case; the meniscus vanishes at about 193° , whilst the level of the mercury only becomes the same in the two arms at 196° . The temperature at which the meniscus disappears is, moreover, not constant; this may be clearly seen by heating a tube of which the two arms contain very different heights of ether, the meniscus may be caused to vanish several times in the one arm without the other meniscus being affected. The author concludes that the temperature at which the meniscus disappears is not constant for the same substance, but depends on the quantity of liquid employed.

W. J. P.

Disappearance of the Meniscus at the Critical Point. By GIULIO ZAMBIASI (*Real. Accad. Lincei*, 1893, i, 21—27).—The author has devised (see preceding abstract) a method by which it may be shown that the temperature of disappearance of the meniscus between a liquid and its vapour enclosed in a tube varies for the same substance. The temperature of disappearance rises as the ratio of the volume of liquid to that of the vapour decreases; the highest temperature at which the meniscus can be made to disappear is the critical temperature, and the substance is then in the critical state. The meniscus disappears at the critical temperature only when the substance has the critical volume, but vanishes below the critical temperature if the total volume is less than the critical volume and greater than the volume which the whole mass would occupy in the liquid state at the same temperature. To raise a substance to the critical state, it is necessary to heat such a quantity that at the critical temperature it will have the critical volume. By using the annular form of tube described by the author, furnished with a regulator of the volume, the substance is in the critical state when the meniscus between the liquid and vapour disappears at the same instant as the level of the mercury in the two arms becomes the same. The space occupied by the substance is then the critical volume, and the temperature and pressure are also the critical ones.

W. J. P.

Gas and Vapour Density Determinations by means of a Pressure Balance. By MAX TOEPLER (*Ann. Phys. Chem.*, 1895, [2], 57, 311—323).—A method is described for determining the density of a gas from the difference in pressure in two capillary tubes open to the atmosphere, one of which is filled with the gas in question and the other with air. H. C.

Extension of the Laws of Gay-Lussac and Avogadro to Homogeneous Liquids and Solid Substances. By ISIDOR TRAUBE (*Ber.*, 1895, 28, 3292—3302).—In a number of previous communications (*Abstr.*, 1895, ii, 70, 308; this vol., ii, 152), the author has shown that, for homogeneous liquids, the molecular volume

$$V_m = \Sigma nC + 25.9,$$

where ΣnC is the sum of the products of the numbers of atoms n_1, n_2, n_3 , &c., and the atomic volumes C_1, C_2, C_3 , &c., and the constant 25.9 is what has been termed the molecular dilatation, and is the same for all substances. For the same pressure and temperature, the molecular volumes of the gases are the same, or $V = \text{constant}$. But, when a gas is under a high pressure or near its point of condensation, as van der Waals has shown, the volume proper of the molecule can no longer be regarded as small in comparison with the intermediate spaces, as is the case with a perfect gas. Avogadro's law for the same temperature and external pressure then becomes

$$V - b = \text{const.}$$

where b is a simple function of the true molecular volume, the value of which, for the perfect gas, becomes zero. A comparison of this formula with that given above shows that the two, if not identical, would, at any rate, become so on sufficient condensation of the gas.

The quantity ΣnC denotes the true volume of the molecule in the narrow sense of the term, and the value of b should, according to theory, be four times the molecular volume; but, as van der Waals has pointed out, as the condensation of the gas increases the value of b diminishes, and, therefore, for liquids, this relationship cannot hold, as the assumption $v > b$ is no longer true. It may, therefore, be maintained that for liquids the constant b is nothing more than the true molecular volume, or ΣnC . The constant $V - \Sigma nC$ acquires, accordingly, a new meaning, and may be termed the "molecular co-volume," so that the observed molecular volume of any compound may be regarded as the sum of two quantities, the true molecular volume, or volume occupied by the molecule, and the molecular co-volume.

It will be seen from the above that Avogadro's law may be applied to both gases and liquids in the form of the general statement, that, under like conditions of temperature and pressure, the volumes in which the molecules are free to move are the same, or the molecular co-volumes are equal.

If Avogadro's law applies to the molecular co-volumes of liquids, the same should be true of Gay-Lussac's law, and the molecular co-volumes of different liquids should expand by equal amounts for the same rise in temperature. To test this conclusion, the author has

calculated the molecular co-volumes at 0° and 100° for a number of the paraffinoid hydrocarbons and for the ethereal salts of some of the fatty acids, these compounds being selected as the disturbing influence of molecular association in the liquid state is thus avoided. The coefficient of expansion, $\alpha = \frac{1}{\text{Cov}_0} \frac{\text{Cov}_{100} - \text{Cov}_0}{100}$, is found to be approximately the same in all cases, and its mean value is 0.00366 or $1/273$. It therefore appears that the molecular co-volumes of the liquids increase by $1/273$ of their value for each degree rise of temperature, and, consequently, that the expansion of liquids like that of gases is proportional to the absolute temperature. The molecular co-volume at any temperature is $24.5 (1 + 0.00366 t)$, or $0.090 T$, the units being grams and cubic centimeters, t temperature in Centigrade degrees, and T the absolute temperature.

As the laws of Avogadro and Gay-Lussac hold for liquids, that of Boyle must, in consequence, be also true, but the present data are insufficient for direct proof. The author shows that there is reason to believe that in the above form these laws may be extended to solid substances, and that the molecular co-volumes are the same in both the liquid and solid states.

The passage from the solid to the liquid state is then unattended by any change in the molecular co-volume, but, in passing from the liquid to the gaseous condition, the molecular co-volume decreases, the decrease being the greater the higher the temperature. There will, therefore, be for every substance a particular temperature at which the molecular co-volumes of the liquid and the gas are the same. This is obviously the critical temperature. H. C.

Degree of Dissociation at Zero Temperature. By R. W. WOOD (*Zeit. physikal. Chem.*, 1895, **18**, 521—523).—The values for the dissociation obtained by the freezing point method are usually lower than those obtained from the conductivity, and Wildermann has suggested that the differences are due to the fact that the conductivity is usually determined at a higher temperature, about 18° to 25° . The author, therefore, determined the conductivity of solutions of potassium chloride at 0° , and the values then obtained for the dissociation, although in almost complete accord with the numbers obtained by Kohlrausch at 18° , are considerably higher than those obtained from the freezing point by Wildermann. The author considers it most probable that, as yet, the freezing point depressions in very dilute solutions are not accurately known. L. M. J.

Determination of Molecular Weights. III. By ERNST BECKMANN, GOTTHOLD FUCHS, and VICTOR GERNHARDT (*Zeit. physikal. Chem.*, 1895, **18**, 473—513; compare *Abstr.*, 1895, ii, 154, 382).—According to Arrhenius' formula, the constant for the boiling point elevation is obtained by the equation $k = 0.0198 T^2/w$, where w is the latent heat of vaporisation of the solvent. This constant is, however, frequently unknown, but may be calculated from Clausius' formula $w = 1.98 T^2 \cdot dp/dt \times 1/Mp$, the letters having their usual significance. Also, by Trouton's rules, which was found to be valid by Juginin

and by Schiff (Abstr., 1895, ii, 154), the latent heat is given by the expression $T/M \times \text{constant}$, the value of the constant varying in different series of compounds. These expressions were tested by the authors for a large number of liquids, the molecular elevation of the boiling point being determined directly and calculated from vapour pressure alteration experiments, as well as by Trouton's rule. The latent heat of vaporisation of the liquid was also calculated, both by the boiling point and vapour pressure determinations. The following liquids were investigated: benzene, cymene, carbon bisulphide, chloroform, methylic iodide, ethylic iodide, ethylic bromide, nitroethane, propionitrile, ethylenic dibromide, ethylenic dichloride; water, methylic, ethylic, propylic, isopropylic, isoamylic, and tertiary amylic alcohols; ether, methylal, methylic and ethylic formate and acetate, isoamylic acetate, paraldehyde, acetone, methyl propyl ketone, camphor, menthone, menthol, and glycerol. In most cases, Trouton's rule gives approximate results, whilst the calculated latent heats agree with one another and with the direct determinations as well as the latter agree among themselves. The values for the latent heat of water obtained by the two methods were 548.8 and 536.8.

L. M. J.

Boiling Points of Solutions of Salts in Methylic and Ethylic Alcohols. By J. WOELFER (*Ann. Phys. Chem.*, 1895, [2], 57, 91—111).—The author has determined the boiling points of dilute solutions of the iodides and acetates of sodium and potassium, the chlorides of lithium and calcium, and the nitrates of silver and calcium in methylic and ethylic alcohols. The molecular weights of the dissolved substances were in each case calculated from the results by means of the formula

$$M = \frac{0.02T^2}{r} \frac{g}{dT},$$

where r is the latent heat of vaporisation of the alcohol, T its boiling point in absolute temperature, dT the raising of the boiling point by the dissolved substance, and g the percentage of the dissolved substance contained in the solution. The calculated molecular weights were found to be almost invariably lower than the true values. They increase, however, with rising concentration, but, in the case of the methylic alcohol solutions, suffer a subsequent decrease when the concentration reaches a certain value. The maximum for the methylic alcohol solutions occurs when the molecular concentration is 0.302 per litre, or, in the case of calcium nitrate, about double this value. The dissociation calculated from the raising of the boiling point, in the case of the ethylic alcohol solutions, only agrees with that determined from the conductivity in the case of the very dilute solutions. In the more concentrated solutions, the dissociation calculated from the boiling points is smaller than that calculated from the conductivities. A better agreement is obtained with the solutions in methylic alcohol. The author's results are not in agreement with Ostwald's law of dilution.

H. C.

Use of Bromoform in Cryoscopy. By G. ANPOLA and C. MANUELLI (*Gazzetta*, 1895, **25**, ii, 91—101).—Bromoform behaves somewhat similarly to benzene and paraxylene (compare Paternò and Montemartini, *Abstr.*, 1895, ii, 207) when used as the solvent in molecular weight determinations by the cryoscopic method. According to Raoult's law, the molecular depression of the freezing point of bromoform should be 156·86; the mean of a number of determinations made with paraldehyde, benzene, naphthalene, paraxylene, thiophen, aniline, dimethylaniline, and quinoline give the value as 144. The substances named in the above list may be said to behave normally towards this solvent; ethylic oxalate gives depressions which are too low, whilst isobutyric and acetic acids, the only two acids studied, give molecular depressions of about half the normal values just as they do in benzene and paraxylene. The behaviour of phenols and alcohols in bromoform is also very similar to their behaviour in benzene and paraxylene; phenol and thymol give low molecular depressions, which decrease rapidly as the concentration increases, until, in a 9 per cent. solution, the molecular depression with phenol is only 53·6. The molecular depressions with ethylic and benzylic alcohols and trimethylcarbinol are low even in 0·5 per cent. solutions, and decrease as the concentration increases until, in a 15·8 per cent. solution, the molecular depression with ethylic alcohol is only 16·2. It is noteworthy that chloroform depresses the freezing point of bromoform normally. W. J. P.

Laws of Connection between the Conditions of a Chemical Change and its Amount. III. Further Researches on the Reaction of Hydrogen Dioxide and Hydrogen Iodide. By A. VERNON HARCOURT and WILLIAM ESSON (*Phil. Trans.*, 1895, **186**, 817—895. Bakerian Lecture).—The investigations commenced nearly 30 years ago by the authors (*Trans.*, 1867, **20**, 460) on the reactions which take place between hydrogen dioxide and hydrogen iodide as a case of gradual chemical change, have been continued at intervals, and the results obtained are communicated in this paper. The vessel employed in making the observations consisted of a tall, glass cylinder, 12 × 3 inches, round which, about 2½ inches from the top, a fine line had been etched. The cylinder was closed by a caoutchouc stopper, through which passed (1) an inverted funnel tube in the centre, (2) a thermometer, (3) a short tube, 1 × ½ inch, giving access to the interior. Into the cylinder were poured water, and measured quantities of solutions of all the reacting substances except hydrogen dioxide; the temperature was brought to the desired degree; and more water was added until the upper surface of the liquid coincided with the line round the cylinder. Then a measure of hydrogen dioxide was brought in. Large bubbles of carbonic anhydride were sent through the liquid to act as a stirrer, the bubbles issuing at the bottom of the inverted funnel. Whenever the liquid, in which iodine was being slowly formed, showed the blue colour of iodised starch, drops of uniform size of a concentrated solution of sodium thiosulphate were brought in one at a time through the short tube. As soon as the small portion of thiosulphate, dis-

solved in each drop, was exhausted, the iodine liberated by the peroxide was no longer removed, the liquid became blue, and the moment of change was noted. Thus were observed the successive intervals required for the performance of a known fraction of the total change, and from these the rate of change was inferred. Such observations furnish the means of measuring the time required for a definite amount of chemical change under known conditions. The time required varies, because one condition is continually varying, namely, the amount of dioxide in the liquid.

If y is the amount of dioxide at a time t , y' at a time t' , the relation connecting these quantities is

$$y' = ye^{-\alpha(t' - t)},$$

in which α is the fraction of the dioxide which disappears in a unit of time. Each observation furnishes a value of α , and the mean of the values obtained in this way from a set of observations is taken as the true value under the conditions of each experiment.

The substances used in most of the observations were (1) a solution containing hydrogen dioxide, made by dissolving sodium dioxide in a slight excess of dilute sulphuric acid; (2) a solution of potassium iodide or hydrogen iodide; (3) dilute sulphuric acid; of the last named, a relatively large quantity being generally taken. The quantities of each substance are stated as the number of millionth-gram molecules per c.c.

The first series of observations were made in order to ascertain the influence on the rate of change of variations in the amount of sulphuric acid. If i denotes the number of millionth-gram molecules of iodide and s the number of millionth-gram molecules of sulphuric acid in 1 c.c., the following three formulæ hold for the solutions examined at 30°

$$\begin{aligned}\alpha &= i\{4730 + 18(s - 190.5)\}10^{-6}, \\ \alpha &= i\{10550 + 22.5(s - 514)\}10^{-6}, \\ \alpha &= i\{16130 + 26.5(s - 762)\}10^{-6},\end{aligned}$$

the first formula holding from $s = 190$ to $s = 514$, the second from $s = 514$ to $s = 762$, and the third from $s = 762$ to $s = 1143$. It appears from this that the increment in the rate of change due to each unit-substitution of sulphuric acid for water is constant until a certain ratio of acid to water is reached; at this point, the increment suddenly rises and remains constant until another ratio of acid to water is reached, after which it again rises and then remains constant as far as the experiments proceeded. These results accord with the view that when a drop of sulphuric acid is mixed with a relatively large volume of water, the liquid consists of a mixture of water with whatever hydrate of the acid contains the largest number of molecules of water. If the addition of acid is continued, the proportion of this first hydrate increases and the proportion of water diminishes, until a point is reached at which the liquid consists of the hydrate. After this point, a new order of events begins; a second hydrate is formed with a larger proportion of acid, its amount increasing and that of the first hydrate decreasing, until the liquid consists of the

second hydrate. Then begins the formation of a third hydrate, and so on.

Sets of observations at the lower temperatures of 16° and 20° , also show that the value of the increment of rate, caused by successive replacements of water by sulphuric acid, changes abruptly at certain points. The results are consistent with the supposition that, at the three temperatures of the authors' experiments, the composition of the two hydrates indicated is the same. Their composition is probably not far removed from $\text{H}_2\text{SO}_4, 106\text{H}_2\text{O}$ and $\text{H}_2\text{SO}_4, 71\text{H}_2\text{O}$, and it may have some significance that these numbers are to one another in the ratio of 3 : 2. The rise of temperature of 14° augments the increment of the rate of change per unit of sulphuric acid in the ratio 2.62 : 1, whichever hydrate is being formed.

Separate investigations were made with the object of ascertaining the effect of the first additions of very small quantities of acid. The first small addition of sulphuric acid causes a much greater increment of the rate than subsequent small additions, and it is only when the proportion of acid reaches a certain limit that the first minimum and constant value of the coefficient of s appears.

The influence of hydrogen chloride on the rate of change was next investigated. Putting i for the number of millionth-gram molecules of hydrogen iodide, and c for the number of millionth-gram molecules of hydrogen chloride, the equation which represents the variation of the rate with the amount of hydrogen chloride, at 30° and over the range of the observations, which were extended from $c = 71$ to $c = 355$, is

$$\alpha = i \{2800 + 16.8(c - 71.1)\} 10^{-6}.$$

Comparing the influence on the rate of the presence of sulphuric acid and hydrogen chloride respectively, it will be seen that, molecule for molecule, the two acids are nearly equivalent, instead of one molecule of sulphuric acid being equivalent to two molecules of hydrogen chloride as in combining with bases.

An addition of hydrogen iodide, like an addition of hydrogen chloride or sulphuric acid, causes an increment in the rate. It is necessary in this case to separate the effect of the hydrogen iodide as one of the substances which is undergoing change from that of the hydrogen iodide as an acid; and when this is done, the numbers found are in arithmetical progression, and correspond with the previous series representing the accelerating effects of sulphuric acid and hydrogen chloride.

The effect of an addition of sodium hydrogen carbonate was also investigated, and here again the results obtained were similar to those given by the other substances examined.

Instead of varying the conditions of the change by taking more or less of some of the ingredients of the solution, it was possible to make a variation by substituting salts with the same metal or acid radicle, one for another, in the proportion of their molecular masses. The effect of substituting sodium for potassium iodide molecules is to increase the rate; a substitution of sodium for hydrogen chloride causes a decrease. The influence of sodium chloride on the rate, and

doubtless that of other salts, is far greater in presence of sodium hydrogen carbonate than it is in presence of hydrogen chloride. A substitution of iodide for chloride, in molecular proportion, causes a retardation; but, absolutely, each salt accelerates.

The results obtained throughout do not seem to show any effect of progressive dilution beyond the necessary consequence that every addition of water diminishes proportionally the mass of each acid or salt in unit volume. If the hypothesis of ionic dissociation is accepted, it seems to follow that the acids and salts which have been the subject of these experiments are either (1) so near complete dissociation in solutions of normal strength that no great increase in the proportion of ions to molecules is caused by further dilution, or (2) that not much dissociation has yet taken place in solutions of less than centinormal strength, or (3) that the ions interact at the same rate, and accelerate chemical change in the same degree, as the molecules from which they are formed.

In order to study the effect of varying the temperature, the rates at different temperatures were compared when the change takes place with the same amounts of each substance in unit volume. A solution containing sulphuric acid and hydrogen iodide was selected for the purpose, and to facilitate the investigation of the law of connection between α and t , a calculation was made, by interpolation from the results, of the rates at degrees of temperature expressed in whole numbers and with successive differences of 5° . The observations extended from 0° to 50° , and the table is given of the values of α , their logarithms to the base 10, and the successive differences of the logarithms, $\Delta \log \alpha$. These last numbers continually diminish as the temperature increases, and as a first approximation may be assumed to be in arithmetical progression; so that we may put $\Delta \log \alpha_x = a - bx$. This formula, however, although convenient for calculating the rates at different temperatures ranging from 0° to 50° would fail for higher degrees of temperature.

A function of x , the successive differences of which closely resemble the successive differences of $\log \alpha$, is $u_x = \log(c + x)$, when c is considerably larger than x . Assuming that

$$\log \alpha_x = m \log \left(\frac{c + x}{c} \right) + \log \alpha_0,$$

the values of m and c may be found from the experimental numbers. If the value of x is taken as 5, that of c is found to be 54.52, or since $5x = t$,

$$\log \alpha_t = m \log \frac{272.6 + t}{272.6} + \log \alpha_0,$$

$$\text{or} \quad \frac{\alpha_t}{\alpha_0} = \left(\frac{272.6 + t}{272.6} \right)^m$$

This equation implies that no chemical change will take place when $t = -272.6$, a temperature at once recognised as practically identical with that of the absolute zero. Thus, within the limits of experimental error, it may be assumed that the zero of chemical change

coincides with the zero of absolute temperature. If we call the absolute temperature at the freezing point T_o , the equation of connection of the amount of chemical change with temperature may be written in the form

$$\frac{\alpha_T}{\alpha_{T_o}} = \left(\frac{T}{T_o} \right)^m$$

The form of this equation shows that the relation between the amount of chemical change at a given temperature and the absolute temperature is independent of the units in which each of these quantities is measured. It is further shown in the paper that the number m , which remains constant in a series of experiments at different temperatures with the same kind of solution, varies with the nature of the main ingredient of the solution, but not with the amount of that ingredient. If α and α' are two rates corresponding with two temperatures very near to each other

$$\frac{\alpha' - \alpha}{\alpha} \cdot \frac{T' - T}{T} = m.$$

which implies that the increase of each unit of chemical change per unit increment of each unit of temperature is constant at all temperatures.

A large number of experimental confirmations of this law of the connection between chemical change and temperature are given in the paper. It is convenient to express the relation in the form

$$\log \alpha - \log \alpha_o = m (\log T - \log T_o).$$

This mode of stating the law has the advantage that the graphic representation is a straight line. H. C.

Stability of Imides of Dibasic Acids. By ARTURO MIOLATI (*Real. Accad. Lincei*, 1894, i, 515—521).—The imides of the dibasic acids are soluble in water, and are slowly decomposed by dilute hydrochloric acid at the ordinary temperature, so that they lend themselves readily to determinations of the velocity of reaction. The reaction is of the second order, and is therefore represented by the usual expression $Ac = x/t(A - x)$, the units being cubic centimetres and minutes. The determinations were made at 25° in 190 c.c. of N/190 solutions of the imide to which 10 c.c. of N/10 caustic soda was added; from this mixed N/200 solution, samples were drawn at definite intervals and the acid determined by titration. The velocity constants, Ac , for succinimide, pyrotartarimide, and glutarimide are 0.002382, 0.001374, and 0.2511 respectively.

It is seen that, by introducing a methyl group into succinimide, and so getting pyrotartarimide, the resistance to hydrolysis is greatly increased; by lengthening the methylene chain by one $-\text{CH}_2$ group, as in glutarimide, the velocity of decomposition becomes a hundred times greater than with the original succinimide. W. J. P.

Stability of Substituted Succinimides. By ARTURO MIOLATI and E. LONGO (*Real. Accad. Lincei*, 1894, i, 597—605).—Using the

method previously described (see preceding abstract), the authors have determined the velocities of hydrolysis of a number of succinimides of the constitution $\begin{matrix} \text{CH}_2 \cdot \text{CO} \\ | \\ \text{CH}_2 \cdot \text{CO} \end{matrix} > \text{NR}$, where R is an alkyl radical; the velocity constants Ac are tabulated below.

R.	Ac.	R.	Ac.
H.....	0·00238	C ₆ H ₅ ·CH ₂ ·	0·276
CH ₃ ·CH ₂ ·CH ₂ ·	0·05500	CH ₂ ·CH·CH ₃ ·	0·282
Et·	0·08500	C ₆ H ₄ Me (para)·	1·120
Me·	0·21700	C ₆ H ₅ ·	2·270

The substances are arranged in order of stability, and, as will be seen, are very much more readily hydrolysed than the unsubstituted succinimide. W. J. P.

Reaction Velocity of Intramolecular Changes in Stereoisomeric Oximes. By HEINRICH LEY (*Zeit. physikal. Chem.*, 1895, 18, 376--398).—The first change studied was that from the syn-aldoxime acetate to the corresponding nitrile and acetic acid. The observations were made at temperatures varying from 25° to 70° in the case of the acetates of thiophen-synalldoxime, anis-syn-alldoxime, benz-syn-alldoxime, parachlor-, parabrom-, and periodo-benz-syn-alldoximes, the compounds being enumerated in the order of magnitude of the reaction constants, which vary from 0·00041 to 0·0007 at 25°, and 0·00296 to 0·012 at 50°, the reaction being of the first order. The results are also shown by curves, in which a specific influence of the thiophen group is evident, the curve for its derivative falling apart from the rest. The temperature influence agrees fairly satis-

factorily with van't Hoff's formula, $K_t = K_o \cdot e^{\frac{T_1 - T_o}{T_1 \cdot T_o}}$.

The next change considered was the intramolecular change from the syn-alldoxime to the anti-alldoxime in alcoholic hydrogen chloride solution. This was done in the case of the benzalldoxime, anisalldoxime, and *p*-chloralldoxime acetates, at temperatures varying from 10° to 40°. The constant was greatest for benzalldoxime, $C_{10} = 0·0148$, and least for anisalldoxime, $C_{10} = 0·0075$, whilst the temperature change is as indicated theoretically.

In this case, the thiophen derivative could not be examined, as, under the conditions of the experiments, the nitrile is produced.

L. M. J.

Action of Unorganised Ferments. By GUSTAV TAMMAN (*Zeit. physikal. Chem.*, 1895, 18, 426--442).—The enzymes differ from inorganic hydrolytic agents in exerting a special, and not a general, action, and also in their loss of activity during the progress of the action. Hence, of two reactions with equal initial velocities, that caused by an enzyme progresses more slowly than that caused by an acid, &c. For the study of this loss of activity, the decomposition of salicin by emulsin was investigated.

Other conditions being similar, the quantity of salicin decomposed in a given time was found to be dependent on, and could be employed as a measure of, the quantity of emulsin present. Emulsin was then dissolved in water, and, from time to time, equal quantities were withdrawn, and the quantity of the active enzyme measured by salicin, as indicated above. At temperatures above 50° , the loss of activity of the emulsin appears to be due to a unimolecular reaction, since the value $1/t \cdot \log 100/(100 - x)$ remains approximately constant, where $100 - x$ is the percentage of active enzyme found in the solution after a given time t ; at temperatures below 50° , however, this expression did not lead to a constant value. The loss of activity of solid emulsin was also determined at temperatures between 80° and 108° , the reaction being again of the first order. The reaction velocity for the decomposition of salicin diminishes, therefore, but the measurement of the initial velocities at 25° and 40° agree well with those calculated from the initial velocity at 0° . The decomposition cannot be complete, but must tend towards a definite limit, which is a function of the original quantities of both salicin and emulsin, varying, from 0 to 1 when the quantity of ferment varies from 0 to 8, and the validity of this deduction is proved experimentally. L. M. J.

Molecular Symmetry and Asymmetry. By ALBERT LADENBURG (*Ber.*, 1895, **28**, 3104—3105; compare *Abstr.*, 1895, ii, 489).—A reply to Groth (this vol., ii, 159). M. O. F.

The so-called Liebig's Condenser. By GEORG W. A. KAHLBAUM (*Ber.*, 1896, **29**, 69—71).—The form of apparatus in general use is a modification of the condenser originally described by Weigel in the year 1771. Liebig simply referred to it (*Handbuch Chem.*, 1843) as a known form, having many advantages. M. O. F.

Modification of Mohr's Balance, and a Simple Apparatus for Measuring the Volumes of Solids. By GIOVANNI GUGLIELMO (*Real. Accad. Lincei*, 1894, ii, 299—303).—The author describes a modification of Mohr's balance for determining densities. The volume of a solid can be determined within 0.01 c.c. by measuring with a burette the volume of water which it displaces from a beaker, the edge of which is ground, and which is furnished with a glass or platinum pointer, terminating in the plane of the edge of the beaker. W. J. P.

Inorganic Chemistry.

Ratio of the Atomic Weights of Oxygen and Hydrogen. By JULIUS THOMSEN (*Zeit. anorg. Chem.*, 1895, **11**, 14—30; see also Abstr., 1894, ii, 277).—The method employed consisted in determining the weight of hydrogen evolved by dissolving a known weight of pure aluminium in sodium hydroxide in a specially constructed appa-

ratus; the weight of hydrogen being determined by the difference in weight before and after the dissolution of the aluminium. Also, in a similar apparatus, by determining the increase in weight brought about by burning the evolved hydrogen in pure oxygen. Drawings and a full description of the apparatus employed are given in the original paper. The mean of 21 experiments, in which altogether 162.3705 grams of aluminium were used and 18.1778 grams of hydrogen evolved, gave hydrogen/aluminium = 0.11190 ± 0.000015 , and the mean of 11 experiments in which 86.9358 grams of aluminium was used and 77.1876 grams of oxygen, gave oxygen/aluminium = 0.88787 ± 0.000018 . Whence $O : H = 15.8690 \pm 0.0022$. Or when $O = 16$, the atomic weight of hydrogen is 1.008255, and the molecular weight of water is 18.0165. These results agree very closely with the recent determinations by other experimenters. E. C. R.

Origin of Atmospheric Oxygen. By THOMAS L. PHIPSON (*Compt. rend.*, 121, 719—721).—See this vol., ii, 265.

Decomposition of some Trinitrides. By ALBERTO PERATONER and GIUSEPPE ODDO (*Gazzetta*, 1895, 25, ii, 13—21).—The molecular weight of argon, 40, approximating to that of a triatomic polymeride of nitrogen, the authors have made a number of experiments on the gas obtained by the decomposition of azoimide and its derivatives, and find that argon is in no case obtained.

During the electrolysis of sodium azoimide solutions, nitrogen and hydrogen are at first evolved in the proportion of 3 : 1, but as the quantity of salt decreases, oxygen and nitrogen collect at the positive pole, although not in quantities equivalent to the hydrogen separated at the negative pole, owing to oxidation of the nitrogen to nitric acid. The same behaviour is observed in the electrolysis of aqueous azoimide; ammonia, but no hydrazine, is found in the residual solution. The irregularities observed by Hittorf during the electrolysis of trinitrides are due to the occurrence of secondary reactions such as are here indicated. The nitrogen obtained on exploding silver trinitride by heat in a special apparatus, and that evolved during the hydrolysis of paranitrotriazobenzene were also examined. The densities of the various samples of gas obtained in these experiments were determined and the gas was sparked after mixing with oxygen; in no case, however, was argon detected or evidence obtained of the existence of the polymeride N_3-N_3 , corresponding with the azoimide radicle.

W. J. P.

Argon. By RAFFAELLO NASINI (*Gazzetta*, 1895, 25, i, 37—46).—The author contends that if the ratio of the two specific heats of an elementary gas such as argon approximates to 1.67, this fact can only be used as confirmatory evidence of the probable monatomicity of the molecules, but cannot be accepted as authoritative and conclusive evidence, if no other facts pointing to the same conclusion are forthcoming. The values of k for all the polyatomic gases are considerably less than 1.67, but the values for the diatomic gases are not all the same, indicating that the approximation to sphericity of the

molecules, or the magnitudes of the intermolecular movements, or both, have different values for different gases; it is thus quite possible that the molecules of argon are diatomic, but so nearly spherical, and possessed of so little internal movement that the value of k is almost that of a monatomic gas. If argon is monatomic, it has an atomic weight of about 40, and finds no place in the recognised periodic classification; if, as seems more probable, it is diatomic and has an atomic weight of about 20, between those of fluorine and sodium, it finds a suitable place in the periodic system as the first member of a new series of elements lying between the series of the halogens and of the alkali metals.

W. J. P.

Solubility of Silica. By ARTHUR M. EDWARDS (*Chem. News*, 1896, **73**, 13).—The siliceous shells of *Bacillariaceæ*, *Spongidae*, and *Radiolariae*, in infusorial earth and soundings are observed to dissolve in fresh spring water, probably from its containing ammonia.

D. A. L.

Italian and other Cements. By GIUSEPPE ODDO and E. MANZELLA (*Gazzetta*, 1895, **25**, ii, 101—113).—The authors have made analyses and resistance tests of a number of hydraulic, Roman and Portland cements of Italian, German, and French origin; the percentage compositions of the Italian cements are not very different from those of the other samples examined. The mean composition of the slowly setting cements in percentages is 61.14 CaO, 1.05 MgO, 20.94 SiO₂, 9.26 Al₂O₃, and 1.5 Fe₂O₃, whilst that of the rapidly setting samples is 57.67 CaO, 0.90 MgO, 21.97 SiO₂, 9.91 Al₂O₃, and 1.46 Fe₂O₃. The molecular compositions of the slowly and rapidly setting cements are respectively

$$\frac{2.183 \text{ CaO} + 0.052 \text{ MgO}}{0.070 \text{ SiO}_2 + 0.182 \text{ Al}_2\text{O}_3 + 0.019 \text{ Fe}_2\text{O}_3} = 2.481$$

and

$$\frac{2.060 \text{ CaO} + 0.045 \text{ MgO}}{0.0732 \text{ SiO}_2 + 0.194 \text{ Al}_2\text{O}_3 + 0.019 \text{ Fe}_2\text{O}_3} = 2.227.$$

The ratios of numerator to denominator are the molecular ratios of basic to acid radicles present, and are considerably lower than the values found by Le Chatelier.

W. J. P.

The Setting of Cements. By GIUSEPPE ODDO and E. MANZELLA (*Gazzetta*, 1895, **25**, ii, 113—127; compare preceding abstract).—Although no noteworthy difference in composition exists between Italian and other cements, there is a very appreciable difference between the behaviour of the two classes of cements towards potassium carbonate. Samples of powdered cements, before and after setting, were extracted for definite times with potassium carbonate solution, using a special form of mechanical agitator, samples of the solution being drawn off at definite intervals, and the total and caustic alkalinity determined. The caustic alkali extracted from the French and German samples of unset cements practically reached a maximum within the first half hour; after setting, however, a much larger

quantity of caustic alkali was extracted and the quantity increased continually as the time of extraction was increased to 9 hours. It is concluded that before the setting of these cements they contain but small quantities of free lime and readily decomposable polysalts; the quantity of these salts, which are slowly and continuously decomposed by potassium carbonate, is much greater after the setting.

Most of the Italian cements contain considerable quantities of lime before setting, and it is concluded that the setting is due to hydration of the salts present, for the amount of caustic alkali extracted by the potassium carbonate solution is not appreciably greater, and sometimes less, after setting, and frequently decreases as the time of extraction is increased.

W. J. P.

Manufacture and Commercial Separation of Beryllium.

By HENRY N. WARREN (*Chem. News*, 1895, **72**, 310—311).—Pulverised and lixiviated emerald is fused for 3 hours in a blast furnace, with four times its weight of sodium carbonate; the solidified mass is decomposed by superheated steam, and then by hydrochloric acid; evaporated to dryness, extracted with water, and the silica separated. The solution, freed from iron and chromium by the acetate method, is first treated with excess of sodium carbonate, and the precipitate heated with excess of sulphurous acid, when the alumina and glucina pass into solution; on boiling, the alumina is precipitated in a granular form, that can be readily washed; excess of ammonium carbonate is then added to the solution, which is well boiled. The precipitate of beryllium carbonate thus obtained is ignited with lamp-black out of contact with the air, and then submitted to the action of bromine vapour at a full red heat in clay retorts. Beryllium bromide distils over, and is reduced electrolytically.

D. A. L.

Sulphur and Carbon in Zinc. By ROBERT FUNK (*Ber.*, 1895, **28**, 3129—3132; compare *Abstr.*, 1895, ii, 390).—The purified zinc of commerce usually contains traces of sulphur and carbon, which are not, however, dissolved in the metal, and may, therefore, be removed from the fused zinc by filtration through asbestos; the odour of the gas evolved by the action of zinc on sulphuric acid is due to the presence of hydrogen sulphide. (Compare this vol., ii, 274).

M. O. F.

Orthoplumbates of the Alkaline Earths. By GEORG KASSNER (*Arch. Pharm.*, 1895, **233**, 501—507).—Calcium orthoplumbate, $\text{Ca}_2\text{PbO}_4 + 4\text{H}_2\text{O}$ (*Abstr.*, 1895, ii, 14) loses $3\text{H}_2\text{O}$ at $240\text{--}250^\circ$, and is converted into a mixture of calcium metaplumbate, CaPbO_3 , and hydroxide, although at a higher temperature (500°) these two substances condense again to the orthoplumbate. Calcium metaplumbate, on ignition, is converted into the orthoplumbate, lead monoxide, and oxygen. Anhydrous calcium metaplumbate is a chocolate brown powder, which, after long contact with water, absorbs $2\text{H}_2\text{O}$, and assumes a lighter hue.

Calcium diplumbate (*loc. cit.*), $\text{CaH}_2\text{Pb}_2\text{O}_6$, loses half its water at

310°, and the remainder at 380—400°. The intermediate product, *calcium tetraplumbate*, $\text{Ca}_2\text{H}_2\text{Pb}_4\text{O}_{11}$, is a loose yellowish powder.

JN. W.

Metaplumbates of the Alkaline Earths. By BRUNO GRÜTZNER and M. HÖHNEL (*Arch. Pharm.*, 1895, **233**, 512—521).—Calcium metaplumbate (preceding abstract) may be prepared by digesting the orthoplumbate with sodium peroxide and water; it is a white powder, crystallising in microscopic cubes. The analyses point to its containing $4\text{H}_2\text{O}$. A less pure product may be obtained by substituting caustic alkali for the alkali peroxide.

Silver metaplumbate, obtained by digesting calcium metaplumbate with aqueous silver nitrate at the ordinary temperature, is a dark gray, silky powder, crystallising in microscopic cubes. The crude product contains silver oxide, which can be dissolved out with ammonia; the product thus purified is of a clear gray colour, and its composition corresponds with the formula Ag_2PbO_3 .

The barium and strontium salts cannot be prepared by the above methods.

JN. W.

Thallous Fluoroxymolybdate and Fluoroxymolybdate.

By FRANCESCO MAURO (*Real. Accad. Lincei*, 1893, ii, 382—384; compare Abstr., 1893, i, 124).—Delafontaine first prepared thallous fluoroxymolybdate, $2\text{TlF}, \text{MoO}_2\text{F}_2$, by dissolving thallous oxide and molybdic anhydride in dilute hydrofluoric acid, but made the erroneous statement that it contains water of crystallisation; it is sparingly soluble in water and forms long, orthorhombic crystals which lose their transparency after a time; $a:b:c = 0.85521:1:1.02474$.

Thallous fluoroxymolybdate, $2\text{TlF}, \text{MoOF}_2$, is prepared by electrolysis a solution of molybdic anhydride in hydrofluoric acid, covered with a layer of petroleum, and adding thallous oxide until the solution is decolorised. The deposited salt crystallises in vitreous, green, orthorhombic plates or prisms; $a:b:c = 0.86595:1:1.02952$.

Monothallous fluoroxymolybdate, $\text{TlF}, \text{MoO}_2\text{F}_2$, which is deposited on concentrating a hydrofluoric acid solution of thallous fluoroxymolybdate over sulphuric acid, crystallises in lustrous, yellow, monoclinic plates which begin to decompose at 240°;

$$a:b:c = 0.61985:1:1.39755. \quad \beta = 86^\circ 7'.$$

It was found by Scacchi (*Real. Accad. Lincei*, 1893, ii, 401) to be isomorphous with monammonium fluoroxymolybdate.

W. J. P.

Action of Phenol on Mercurous Iodide. By MAURICE FRANÇOIS (*Compt. rend.*, 1895, **121**, 768—770).—Mercuric iodide dissolves somewhat readily in hot phenol and separates in the yellow modification, which only slowly changes into the red form.

Boiling phenol decomposes mercurous iodide into the mercuric salt, which dissolves, and mercury which remains undissolved. The decomposition is however limited, and equilibrium is established when the phenol contains 2.75 parts of mercuric iodide in 100. A solution containing a higher proportion of mercuric iodide will attack mercury with formation of the mercurous salt, this action continuing in

presence of excess of mercury, until the proportion of mercuric iodide in solution is reduced to 2.75 parts in 100°. Mercurous iodide is only very slightly soluble in boiling phenol in presence of sufficient mercuric iodide to prevent decomposition, but the mercurous iodide which has been heated to 100° in presence of phenol is converted into very distinct though microscopic crystals. (Compare this vol. i, 22). C. H. B.

Probable New Element in Terbia. By PAUL LECOQ DE BOISBAUDRAN (*Compt. rend.*, 1895, **121**, 709).—A deep red-brown terbia when dissolved in hydrochloric acid showed only a faint absorption spectrum of dysprosium, and a nebulous band at $\lambda 487.7$ which does not coincide with any known band, but seems to belong to a new element which the author distinguishes as $Z\delta$. C. H. B.

Manganese Silicide. By VIGOUROUX (*Compt. rend.*, 1895, **121**, 771—773).—Manganese silicide, SiMn_2 , is obtained (1) by heating silicon with nine times its weight of manganese in the electric furnace and treating the product first with water, then with dilute hydrochloric acid, and finally, and rapidly, with dilute hydrofluoric acid, or (2) by heating in the electric furnace a mixture of 1 part of silica, 3 parts of manganoso-manganic oxide, and 1 part of sugar-carbon, and treating the product as above, or better, (3) by heating silicon with 4 or 5 times its weight of manganoso-manganic oxide in a porcelain dish in an atmosphere of dry hydrogen up to the softening point of porcelain.

It has a metallic lustre and a steel-grey colour, is very hard and very brittle, and perfectly crystallised; sp. gr. = 6.6 at 15°. It does not alter when exposed to air, and melts at the temperature of the reverberatory furnace. Fluorine attacks it at the ordinary temperature, chlorine at about 500°, and iodine and bromine at higher temperatures; oxygen and air attack it at a red heat. Dry hydrogen fluoride decomposes it readily, especially if gently heated, hydrogen chloride below a red heat, and hydrogen iodide at a higher temperature; water is without action at 100°, but at a red heat decomposes the silicide, with liberation of hydrogen. Dilute acids attack it readily, and concentrated acids, especially hydrofluoric acid, are violent in their action; aqueous potash is without effect, but the solid substance attacks the finely powdered silicide when heated with it, and fused alkali carbonates or mixtures of carbonate and nitrate oxidise it readily. C. H. B.

Electro-dissolution and its Uses. By HENRY N. WARREN (*Chem. News*, 1896, **73**, 37—38).—When iron containing boron, silicon, sulphur, phosphorous or carbon is the positive electrode, platinum being the negative in a bath of sulphuric acid, the iron dissolves, whilst the impurities are wholly or partly precipitated. With impure copper in a hydrochloric acid bath, the copper is precipitated on the platinum, whilst the impurities—arsenic, iron

zinc, &c., remain in solution. Stannic nitrate, potassium ferrate, and ferric acetate may be prepared by electro-dissolution.

D. A. L.

Hydrolytic Decomposition of Ferric Chloride. By UBALDO ANTONY and G. GIGLIO (*Gazzetta*, 1895, 25, ii, 1—12).—Freshly prepared and perfectly neutral ferric chloride solutions were made by digesting precipitated ferric hydroxide with dilute hydrochloric acid in the cold, filtering from the excess of ferric hydroxide, and subsequently adding the requisite quantity of hydrochloric acid to give a pure solution of FeCl_3 . Those which contain less than 1.1 per cent. of the salt appear colourless in a 40 centimetre tube, but after several hours become yellow, the colour increasing in intensity during 48 hours after preparation. Dilute solutions, which have been preserved for some days, only slowly give a blue colour with ferrocyanide, whilst a solution containing only 0.00083 per cent. of ferric chloride gives no colour with ferrocyanide. From these results, and from the behaviour of the solutions towards sodium chloride and hydrogen sulphide, it is concluded that the ferric chloride reacts with the water, being converted in infinitely dilute solutions, or those containing less than 0.00083 per cent., into colloidal ferric hydroxide, which is not acted on by potassium ferrocyanide; it is further shown by colorimetric measurements that the velocity of the reactions does not stand in simple relation to the concentration of the solution, so that it must be assumed that the hydrolysis leads to the formation of intermediate products, like $\text{FeCl}_2(\text{OH})$ and $\text{FeCl}(\text{OH})_2$. In the more concentrated solutions, a stable equilibrium is set up between these basic compounds and the other constituents of the solution; this equilibrium is destroyed by the addition of ferrocyanide, which only reacts with the ferric chloride, thus causing the hydroxy-chlorides to be acted on by the acid present, again yielding ferric chloride.

W. J. P.

Salts of Ferric acid. By LUDWIG MOESER (*Arch. Pharm.*, 1895, 233, 521—527).—Potassium ferrate is best prepared by gradually adding bromine (50 grams) to ferric hydroxide (80—90 grams) suspended in a cooled concentrated caustic potash (50 grams in 80 grams of water); more potash is then added, and the mixture warmed and kept at 50—60° for half an hour. The cooled ferrate is drained on a tile, and the excess of alkali removed by alcohol; the potassium bromide is then removed by dissolving the product in a little water and reprecipitating it with alcohol. Potassium ferrate is a reddish-black powder, very soluble in water, forming a deep red solution. When ignited, it loses oxygen, and is converted into the green ferrite, which, unlike it, is very deliquescent, and rapidly oxidises to potassium and ferric hydroxides when exposed to air. Potassium ferrate is converted by alkali sulphides into a green substance, possibly a sulphoferrate.

Barium ferrate is obtained as a dark crimson, amorphous powder by precipitating potassium ferrate with barium chloride. It is also prepared by boiling freshly precipitated ferric hydroxide with baryta water and an appropriate oxidising agent, such as barium hypochlorite. Barium ferrate, on ignition, is decomposed into barium ferrite, water,

and oxygen, and is violently acted on by acids, evolving oxygen, and yielding barium and ferric hydroxides; if nitric or sulphuric acid is used, the oxygen contains much ozone. Barium ferrate may be reconverted into an alkali ferrate by digestion with the alkali carbonate, and in this way *rubidium* and *cæsium* ferrates may be obtained.

JN. W.

Platosomonodiamine Compounds. By ALFONSO COSSA (*Real. Accad. Lincei*, 1894, ii, 360—362).—On heating aqueous platosodiamine chloride with hydrochloric acid for some hours, platososemidiamine chloride separates; on adding potassium platinosochloride to the filtrate, the undecomposed platosodiamine chloride is immediately deposited as Magnus' green salt, and after filtering and concentrating the solution, platosomonodiamine platinosochloride, $2\text{Pt}(\text{NH}_3)_3\text{Cl}_2, \text{PtCl}_2$, separates in uniaxial, red laminæ of somewhat metallic lustre. It is dissolved by ammonia, with formation of platosodiamine chloride, and with nitric acid yields *chloroplatinomonodiamine nitrate*, which is colourless, and very insoluble in water.

Platosomonodiamine chloride is best prepared by adding the equivalent proportion of platosodiamine chloride to the platinosochloride; on concentrating the solution, Magnus' green salt separates, and on evaporating the filtrate a residue of *platosomonodiamine chloride* is obtained; this crystallises in colourless, monoclinic prisms, and is very soluble in water.

W. J. P.

Mineralogical Chemistry.

Platinum, Pickeringite, and Magnesia zinc alum from N.S.W.

By GEORGE W. CARD (*Records Geol. Survey, N.S. W.*, 1895, **4**, 130—134).
 —*Platinum* as grains from the alluvial gold works of Fifield, Forbes,
 gave, on analysis by J. C. H. Mingaye,

Pt.	Ir.	Rh.	Pd.	Osmiridium.	Fe.	Cu.
75·90	1·30	1·30	trace	9·30	10·15	0·41
		Au.	Pb.	Insoluble.	Total.	
		nil	trace	1·12	99·48	

Pickeringite, occurring as silky, acicular crystals at Mt. Victoria,
 gave

H ₂ O.	Al ₂ O ₃ .	Fe ₂ O ₃ .	FeO.	CaO.	MgO.	K ₂ O.
37·23	10·65	1·27	trace	nil	2·38	0·74
	Na ₂ O.	SO ₃ .	Insol. (sand).	Total.		
	trace	30·28	17·89	100·44		

The magnesia is too low for pickeringite.

Magnesia zinc alum, from New England, gave

Al ₂ O ₃ .	FeO.	ZnO.	CuO.	MgO.	Na ₂ O.	K ₂ O.	SO ₃ .	P ₂ O ₅ .	Insol.	H ₂ O [diff.].
9.36	trace	3.34	trace	5.78	0.60	trace	34.62	0.28	2.51	[43.51]

L. J. S.

Analyses of Gold, Meerschaum, Amber, and Magnetite from Servia. By SIMA M. LOZANIĆ (LOSANITSCH) (*Ann. Géol. Pénins. Balkan.*, 1893, **4**, (2), 81—86).—Gold from Slatina gave, Au 89.39; Ag 9.20; sand, traces; = 98.59. Meerschaum from Zlatibor gave

SiO ₂ .	MgO.	FeO.	Loss on ignition.	Total.
53.89	22.83	0.88	22.20	99.80

Amber from Vranješ, Kraljevo, of hardness 2—2.5, sp. gr. 1.081, gave C, 78.16; H, 10.13; O, 11.71 = 100.00.

Analyses, mainly technical, are given of various ores and coals; the following is of magnetite from Venčac.

Insol.	Fe ₂ O ₃ .	FeO.	Cr ₂ O ₃ .	Al ₂ O ₃ .	MgO.	Loss on ignition.	Total.
11.63	60.34	7.92	4.49	4.44	5.44	5.46	99.77

L. J. S.

Analyses of Austrian Minerals, &c. By CONRAD VON JOHN and C. F. EICHLEITER (*Jahrb. k. k. geol. Reichsanst., Wien*, 1895, **45**, 1—28).—Numerous analyses, mainly technical, are given of coals, ores and impure minerals, rocks, mineral waters, and some artificial alloys.

L. J. S.

Vanadiferous Coal from Peru. By TORRICO Y MECA (*Berg- und hütt. Zeit.*, 1895, 361; from *Boletín de Minas*, 1894, December 31).—This coal, from Yauli, resembling anthracite in appearance, was examined for platinum, but with a negative result. One sample gave 1.2 per cent. of a greenish-yellow ash, which contained 38 per cent. of vanadic acid; the blue sulphuric acid solution contained, besides vanadium, small quantities of alumina, lime, and magnesia, and a little nickel. Molybdic and tungstic acids were not found.

L. J. S.

Burmite, a New Amber-like Resin from Upper Burma. By OTTO HELM (*Records Geol. Survey, India*, 1892, **25**, 180—181; 1893, **26**, 61—64; and *Schriften Ges. Danzig*, 1894, **8**, 63—66).—This new fossil resin is semi-transparent, and varies in colour from pale yellow to reddish and dirty brown, whilst some specimens are ruby-red and transparent; it shows a fine blue fluorescence. The shiny conchoidal fracture has a greasy touch. The darker, clouded specimens, of slightly higher specific gravity, enclose particles of organic matter and veins of calcite. A brown, weathered crust is usually present. The hardness of 2.5—3 is slightly higher than that of Baltic amber (succinite); sp. gr. 1.030—1.095. By dry distillation, it decomposes without fusion, yielding white aromatic fumes, a brownish-yellow oil, and a little watery liquid, the latter containing formic acid and probably pyrogallol. Analysis gave

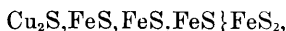
C.	H.	O.	S.	Total.
80·05	11·50	8·43	0·02	100·00

The ash in a pure piece amounted to 0·2 per cent., and consisted of calcium sulphate and carbonate and ferric oxide; an impure specimen gave 4·6 per cent. of ash. It is very resistant to solvents; oil of turpentine dissolving 18·5 per cent., other solvents much less; it is gradually dissolved by concentrated sulphuric acid, yielding a red-brown solution. Burmite is distinguished from the Baltic succinite by the absence of succinic acid; from the Sicilian simetite by its resistance to solvents; and from the Auckland ambrite by its low percentage of oxygen and smaller solubility in carbon bisulphide.

The name burmite was first proposed by F. Noetling (*Records Geol. Survey, India*, 1893, 26, 31), who describes the mode of occurrence and mining of the mineral near Maingkhwan, in the Hukong Valley.
L. J. S.

Composition and Constitution of Cubanite (Cupropyrrite).

By R. SCHNEIDER (*J. pr. Chem.*, 1895, [2], 52, 555—559).—The author's analyses of this mineral are in accord with the empirical formula CuFe_2S_3 , and agree with those of Scheidhauer (*Ann. Phys. Chem.*, 1845, 64, 280). If the rational formula be



the mineral may be regarded as the analogue of sternbergite, $\text{Ag}_2\text{S}, \text{FeS}, \text{FeS}, \text{FeS} \} \text{FeS}_2$, and of a number of sulpho-salts, which the author has from time to time described, of the general form $\text{X}''\text{S}, \text{X}''\text{S}, \text{X}''\text{S}, \text{X}''\text{S} \} \text{Z}^{\text{iv}}\text{S}_2$ where X is a bivalent group or element, and Z a quadrivalent group or element. Several examples are quoted.

A. G. B.

Artificial Precious Opal. By GIUSEPPE CESÀRO (*Jahrb. f. Min.*, 1895, ii, Ref. 8; from *Bull. Acad. Belg.*, 1893, [3], 26, 721—730).—A glass flask, which had contained hydrofluosilicic acid for several years, was coated with a white, translucent, opal-like deposit; this showed a play of colours, and had the composition $3\text{SiO}_2, \text{H}_2\text{O}$. Sodium and calcium silicofluorides were also formed by the action of the acid on the glass.
L. J. S.

Emery from Naxos. By GUSTAV TSCHERMAK (*Tsch. Min. Mitth.*, 1894, 14, 311—342).—The emery of Naxos, an island in the Grecian Archipelago, occurs as lenticular masses in the granular limestone associated with gneiss and schist; it consists, as seen in thin sections, principally of corundum and magnetite, with a little secondary hæmatite and limonite, and some margarite, tourmaline, muscovite, chloritoid, diaspore, and, less frequently, kyanite, staurolite, biotite, rutile, spinel, idocrase, and pyrites. There is a more or less banded structure marked out by layers of the iron ore. The corundum is mostly as rounded grains, but sometimes as crystals when surrounded by magnetite, and it is rich in enclosures, principally of magnetite. Analyses by E. Ludwig gave I for quality A from Kremnó, and II for quality B from Renidi.

	SiO ₂ .	B ₂ O ₃ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	MgO.	CaO.	Na ₂ O.	K ₂ O.
I.	5·64	1·15	57·67	33·36	0·83	0·43	n.d.	0·31
II.	5·45	0·88	56·52	34·65	0·43	0·90	0·60	0·40

	TiO ₂ .	CO ₂ .	Loss on ignition.	Total.
I.	n.d.	—	0·70	100·09
II.	n.d.	n.d.	0·42	100·25

From these analyses is calculated

	Corundum.	Magnetite.	Tourmaline.	Chloritoid.	Muscovite.	Margarite.	Calcite.
I.	52·4	32·1	11·5	—	2	2	—
II.	50	33	9	4	3	—	1

The emery of each deposit is described in detail. The sp. gr. varies from 3·71 to 4·07.
L. J. S.

Magnetite from the Madras Presidency, containing Manganese and Aluminium. By THOMAS H. HOLLAND (*Records Geol. Survey, India*, 1893, **26**, 164—165).—A granular specimen of magnetite, with a distinct reddish streak, and sp. gr. 5·045, from the Kodūr mines, Vizagapatam district, gave, on analysis,

Moisture below 105°.	H ₂ O on ignition.	Insol. in HCl.	Al ₂ O ₃ .	Fe ₂ O ₃ .	Mn ₂ O ₄ .	Total.
0·14	2·18	0·11	2·52	91·62	3·00	99·57

L. J. S.

Artificial Hämatite and Magnetite. By WILHELM MÜLLER (*Zeit. deutsch. geol. Ges.*, 1893, **45**, 63—68).—The residue obtained on reducing nitrobenzene to aniline by means of iron and hydrochloric acid is allowed to stand in heaps before being smelted at Laar, near Ruhrort. Owing to the energetic oxidation of the ferrous chloride, there is a considerable rise in temperature, sometimes to glowing, and the substance becomes a dark, hard, compact mass of iron oxides, the numerous cavities being lined with well-developed crystals (to 1 cm. diam.) of hæmatite and small octahedra of magnetite. Although the hæmatite crystals have all been formed under the same conditions (which are very similar to those in volcanic sublimations, as at Vesuvius), they vary considerably in habit, being tabular, rhombohedral, pyramidal, or prismatic. Analyses of the crystals by Löschner gave Fe₂O₃ 87·38, FeO 12·45 = 99·83; and Fe₂O₃ 86·45, FeO 11·78 = 98·23 per cent.; this indicates an intergrowth of magnetite with the hæmatite, as is also shown by the fact that the crystals are somewhat magnetic. The magnetite gave Fe₂O₃ 71·18, FeO 28·72 = 99·90 per cent.
L. J. S.

Analyses of Magnesite, Dolomite, Mica, and Magnetite from Servia. By A. STANOJEVIĆ (*Ann. Géol. Pépins. Balkan.*, 1893, **4**, (2), 86—88).—Magnesite (I) and dolomite (II) from Avala gave

	SiO ₂ .	FeO.	CaO.	MgO.	CO ₂ .	Total.
I.	0·17	0·66	—	46·60	52·21	99·64
II.	4·37	3·97	24·12	22·25	45·90	100·61

White mica from near Vranja gave

SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	MgO.	K ₂ O.	H ₂ O.	Total.	Sp. gr.
48·93	34·60	3·22	0·63	8·76	5·17	100·68	2·7

Iron ore of sp. gr. 5·01, from Suvo Rudisté (Kopaonik), gave

Insol.	CuO.	MgO.	Fe ₂ O ₃ .	FeO.	CO ₂ .	Total.
1·59	4·03	0·80	67·37	27·63	0·11	101·53

Analyses of other Servian ores are given.

L. J. S.

Iglesiasite, Tarnowitzite, and Hemimorphite from Silesia.

By HERMANN TRAUBE (*Zeit. deutsch. geol. Ges.*, 1894, **46**, 57—67).—*Iglesiasite* occurs on smithsonite at Radzionkau, in comb-like aggregations; analysis gave

PbO.	ZnO.	CO ₂ [diff.].	ZnCO ₃ .	Sp. gr.
78·65	3·41	[17·94]	5·47	6·187

The crystals are flattened in the direction of the vertical (*c*) axis; $a : b : c = 0·59906 : 1 : 0·72465$. $2E_{Na} = 17^{\circ} 7'$.

Tarnowitzite: Analyses of specimens from Tarnowitz gave

	CaO.	SrO.	PbO.	ZnO.	CO ₂ [diff.].	PbCO ₃ .
Colourless.....	54·09	0·28	2·24	—	[43·39]	2·61
Green	52·70	0·25	4·26	—	[42·71]	5·09
Reddish-brown ...	51·93	0·35	4·76	0·34	[42·62]	5·70
Yellowish.....	53·43	trace	3·58	—	[42·99]	4·29

No connection can be traced between the composition and the colour. The crystals used in the last analysis have the habit of aragonite rather than of witherite.

Hemimorphite, from Scharley, was analysed on account of the unusual dark brownish-red colour; lead has not before been recorded in this mineral.

SiO ₂ .	ZnO.	PbO.	H ₂ O.	Total.	Sp. gr.
24·81	66·28	2·17	7·39	99·65	3·627

Crystallographic determinations are given of the above, and of good crystals of hemimorphite from Radzionkau, and of cerussite from Tarnowitz.

L. J. S.

Spodiosite from Nordmark. By GUSTAF NORDENSKIÖLD (*Jahrb. Min.*, 1895, ii, Ref. 18; from *Geol. För. Förh.*, 1893, **15**, 460—466).—Spodiosite occurs as large, orthorhombic crystals, with chondrodite, amphibole, magnetite, and calcite in serpentine veins at Nordmark, Sweden. The freshest portion of the much decomposed mineral gave on analysis

P ₂ O ₅ .	SiO ₂ .	CaO.	Al ₂ O ₃ .	Fe ₂ O ₃ .	MgO.	F.	H ₂ O.	Total (less O for F).
29·62	8·74	45·84	2·83		8·56	2·94	3·76	100·60

As the SiO_2 and MgO belong to the serpentine, the formula becomes $m\text{Ca}_3\text{P}_2\text{O}_8 + n\text{CaF}_2$, where $m = 8$ and $n = 3$, this being analogous to apatite.

L. J. S.

Celestite from Bourke, N.S.W. By GEORGE W. CARD (*Records Geol. Survey, N.S.W.*, 1893, **3**, 201—203).—A soft mass of sp. gr. 3.73 consisting of an aggregation of small crystals, gave, on analysis by J. C. H. Mingaye,

SrSO_4 .	CaSO_4 .	BaSO_4 .	SiO_2 .	Fe_2O_3 (Al_2O_3).	MgO .	NaCl .	H_2O .	Total.
93.57	0.99	trace	3.22	1.52	0.33	trace	0.70	100.33

L. J. S.

A supposed Sulphocarbonate of Lead. By P. T. HAMMOND (*Records Geol. Survey, N.S.W.*, 1895, **4**, 163—166).—White to colourless, brittle, orthorhombic crystals, with an imperfect cleavage, and an adamantine to resinous lustre, found on cerussite from Broken Hill, N.S.W., gave, on analysis by J. C. H. Mingaye,

PbO .	SO_3 .	CO_2 .	Total.
74.11	22.27	3.32	99.70
74.11	25.00	1.34	100.45

There is an absence of water; sp. gr. 6.22—6.33. The crystals differ in many points from leadhillite, and are probably anglesite, containing admixed cerussite, the latter possibly being due to the alteration of the former.

L. J. S.

Zinciferous Melanterite, Seelandite and "Zinkmanganerz." By AUGUST BRUNLECHNER (*Jahrb. naturhist. Landes-Museums, Klagenfurt*, 1893, Heft **22**, 186—194).—Numerous minerals recently found in Carinthia are shortly described.

Melanterite (zinciferous) as small stalactites incrusting dolomitic limestone from Raibl, gave, on analysis,

FeO .	ZnO .	SO_3 .	H_2O .	Total.
20.69	6.01	28.95	44.35	100.00

Seelandite: Colourless, white, or yellowish-white needles, occurring as an efflorescence on siderite from Lölling, gave

MgO .	Al_2O_3 .	SO_3 .	H_2O .	Total.
4.07	10.54	34.03	51.22	99.86

thus corresponding with the formula $\text{MgAl}_2(\text{SO}_4)_4 + 27\text{H}_2\text{O}$. [This is near to pickeringite; seelandite is a new name (see "*Carinthia*," ii, 1891, No. 2).]

"*Zinkmanganerz*": This "new species" occurs as a thin, dull, compact layer of reddish-brown or blackish-brown to steel-grey colour, in hemimorphite druses, or coating hydrozincite at Bleiberg. Streak, dark reddish-brown; fracture, even to flat, conchoidal. Given as a zinc manganite containing water.

Analyses of an impure limonite and a bituminous dolomitic limestone are also given.

L. J. S.

Kentrolite from Jakobsberg. By GUSTAF NORDENSKIÖLD (*Jahrb. f. Min.*, 1895, ii, Ref., 241; from *Geol. För. Förh.*, 1894, **16**, 153—158).—Small, dark reddish-brown to black, orthorhombic crystals on inesite from Jakobsberg, Sweden, gave, on analysis,

SiO ₂ .	PbO.	Mn ₂ O ₃ .	Fe ₂ O ₃ .
16	50	19	1

L. J. S.

Action of Water on Apophyllite. By GIORGIO SPEZIA (*Jahrb. f. Min.*, 1895, ii, Ref., 242; from *Atti Accad. Sci., Torino*, 1895, **30**, 455—465).—Water under a pressure of 1750 atmospheres at the ordinary temperature had no action on apophyllite from Poonah; under a pressure of 500 atmospheres at 93—107° there was no marked action; but water at 190—211°, and under the normal pressure for that temperature, strongly corroded the mineral in 13 days, producing beautiful etch-figures. Glass behaves in a similar manner.

L. J. S.

Lepidomelane, Actinolite, Andradite, Grossular, Hornblende, Clinocllore, Talc, Diallage, Damourite, Sericite, Cookeite, Cobaltiferous Löllingite, Bismuthite, Strontianite, and Native Iron from Canada. By G. CHRISTIAN HOFFMANN (*Report Geol. Survey, Canada*, 1895, **6**, R., 1—93).—*Lepidomelane* (I), brilliant, black plates in a granular mispickel at Marmora, Hastings Co., Ontario.

Actinolite (II), light greenish-grey, finely fibrous, from Westmeath, Renfrew Co., Ontario.

Andradite (III), massive, black, in thin splinters dark purple-red, from Cawood, Quebec; (IV), clove-brown, massive, from Fraser River, B.C.

Grossular (V), massive, honey-yellow, from Litchfield, Quebec.

Hornblende (VI), finely fibrous, radiated, blackish-green, from Fraser River, B.C. Analyses I to VI by F. G. Wait.

	I.	II.	III.	IV.	V.	VI.
SiO ₂	32·79	56·70	36·09	34·52	36·80	38·79
Al ₂ O ₃	14·34	1·62	12·69	4·09	20·53	11·51
Fe ₂ O ₃	4·52	3·06	12·33	25·82	2·38	16·88
FeO	26·32	7·19	3·30	2·66	0·56	15·96
MnO	0·29	0·30	0·48	0·94	0·50	0·62
NiO	—	0·54	—	—	—	—
CaO	1·45	10·62	34·46	31·49	37·41	11·57
MgO	4·68	17·20	0·94	0·59	1·51	2·86
K ₂ O	7·24	0·24	—	—	—	1·36
Na ₂ O	2·00	0·64	—	—	—	0·71
TiO ₂	0·92	—	—	—	—	—
H ₂ O (at 100°)	1·38	0·64	0·04	0·03	0·07	0·09
H ₂ O (above 100°).	3·68	2·05	—	—	—	0·83

99·61 100·80 100·33 100·14 99·76 101·18

Sp. gr. 3·19 2·941 3·690 3·706 3·623 3·404

Clinocllore (VII), white or faint bluish-white, scaly, from a scapo-

lite-serpentine rock at Buckingham, Quebec, ; sp. gr. 2·631. (VIII), dark green, broadly foliated, from Bagot, Renfrew Co., Ontario. Both analyses by R. A. A. Johnston.

	SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	FeO.	Cr ₂ O ₃ .	MgO.	K ₂ O.	H ₂ O.	Total.
VII.	28·65	18·96	—	—	—	37·49	—	15·22	100·32
VIII.	27·23	19·44	2·17	4·91	0·99	32·67	0·08	12·04	99·53

Talc (IX), pale yellowish-green, foliated, from Grimsthorpe, Ontario; water at 100°, 0·32 per cent.; above 100°, 5·42. Analysis by Wait.

Diallage (X), thin-foliated, light greenish-grey, in serpentine, from Melbourne, Quebec.

Damourite (XI), scaly, yellowish-green, in a ferruginous dolomite, from Kicking Horse Valley, B.C. Over sulphuric acid, 0·68 per cent. of water was lost; at 100°, 0·03; on ignition, 5·54, = 6·25 per cent.

Sericite (XII), small, yellowish-white scales, forming 61·64 per cent. of a sericite-schist from Wait-a-bit Creek, Columbia River, B.C. Analysis was made on the portion of the rock insoluble in hydrochloric acid, the soluble portion consisting mainly of carbonates.

Cookeite (XIII), white or pale green, and foliated; occurs as thin bands in the sericite-schist above mentioned. Analyses X to XIII by Johnston.

	IX.	X.	XI.	XII.	XIII.
SiO ₂	60·45	50·66	44·28	46·05	32·00
Al ₂ O ₃	0·27	4·47	33·60	38·36	45·87
Fe ₂ O ₃	0·78	0·70	0·62	0·97	—
FeO	2·04	2·75	—	—	—
Cr ₂ O ₃	—	1·40	—	—	—
NiO	0·50	—	—	—	—
CaO	0·16	21·81	—	2·49	1·63
MgO	29·84	17·45	3·03	0·47	0·78
K ₂ O	—	—	9·87	6·19	0·06
Na ₂ O	—	—	0·40	2·98	0·65
Li ₂ O	—	—	—	0·34	2·10
Cs ₂ O	—	—	—	0·03	—
H ₂ O	5·74	0·69	6·25	2·48	17·29
F	—	—	0·59	—	0·02
Cl	—	—	0·51	—	—
	99·78	99·93	99·13	100·27	100·40
Less O for F	—	—	0·36	—	0·01
Sp. gr.	2·65	3·238	2·857	—	—

Cobaltiferous Löllingite, massive, steel-grey, with pyrrhotite, from Galway, Ontario. Analysis by Johnston gave, after deducting 1·69 per cent. of quartz,

As.	S.	Fe.	Co.	Ni.	Total.	Sp. gr.
70·85	0·81	24·67	2·88	0·79	100·00	7·028

Bismuthite, massive and foliated, lead-grey, from a granite vein at Jonquière, Quebec. Analysis by Johnston gave

Bi.	S.	Fe.	Pb.	Cu.	Total.	Sp. gr.
79.28	18.46	0.74	1.68	0.48	100.64	6.781

Strontianite, radially crystalline, pale yellowish-green to white, as veins in limestone at Nepean, Ontario. Analysis by Johnston gave

CO ₂ .	SrO.	CaO.	Insol.	Total.	Sp. gr.
30.54	65.43	3.38	0.17	99.52	3.704

Native iron occurs as small spherules, very similar to those previously described by the author (Abstr., 1895, ii, 20) in kaolin and limonite in a pegmatite vein at Cameron, Ontario. Analysis by Johnston gave

Fe.	Mn.	Ni.	S. P.	Organic matter.	Insol.	Total.	Sp. gr.
90.45	0.75	trace	not det.		7.26	98.46	7.257

Copper and cobalt are absent. On dissolving in hydrochloric acid, there is a strong smell of phosphine. The insoluble concretionary nuclei contain 88.77 per cent. of silica, with some Al₂O₃, Fe₂O₃, and CaO.

The report also contains numerous analyses of ores, waters, &c.

L. J. S.

Xiphonite, a New Amphibole [Hornblende] from Etna. By GAETANO PLATANIA (*Jahrb. f. Min.*, 1895, ii, Ref., 236—237; from *Atti rend. Accad. Sci., &c., di Acireale*, 1893, N. Ser., 5, 55—62).—This occurs as small, light yellow to honey-yellow, transparent, monosymmetric crystals in the drusy cavities of a slaggy lava. It is supposed, together with the accompanying hæmatite, to have been formed by sublimation. On account of the feeble pleochroism, the light colour, and the special mode of occurrence, it is considered to be a distinct variety of hornblende.

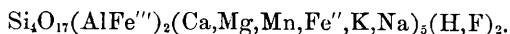
L. J. S.

Chemical Composition and Constitution of Vesuvians [Idocrase] and Wiluite. By PAUL JANNASCH and P. WEINGARTEN (*Zeit. anorg. Chem.*, 1895, ii, 40—48; see also Abstr., 1895, ii, 319).—The paper contains the results of the complete analysis of (I) idocrase from Vesuvius, free from fluorine, of (II) idocrase from the same locality, containing fluorine, and (III) of idocrase from the Matterhorn.

	SiO ₂ .	TiO ₂ .	Fe ₂ O ₃ .	Al ₂ O ₃ .	FeO.	CaO.	MnO.	MgO.	K ₂ O.
I.	36.38	4.28	2.77	12.29	2.14	35.56	0.37	2.94	0.42
II.	37.15	0.50	3.28	15.73	1.94	35.49	0.52	2.64	0.38
III.	37.09	2.15	3.59	15.56	0.83	35.24	0.18	2.24	0.72

	Na ₂ O.	H ₂ O.	F.	Total.
I.	0.95	2.68	—	100.78
II.	0.67	1.97	1.63	101.95
III.	0.53	2.71	—	100.84

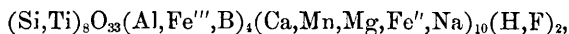
The results obtained agree with the former determinations, and are in accordance with the composition



A complete analysis of wiluite gave

SiO_2 .	TiO_2 .	B_2O_3 .	Fe_2O_3 .	Al_2O_3 .	FeO .	CaO .	MnO .	MgO .
36.01	1.30	2.81	2.18	12.23	1.49	35.81	0.15	6.05
		Na_2O .	Fl.	H_2O .	Total.			
		0.45	0.22	1.34	100.04			

from which the formula,



is deduced.

E. C. R.

Origin and Composition of Onyx Marbles. By GEORGE P. MERRILL (*Smithsonian Report, U.S. National Museum*, for 1893-4, 1895, 539-585).—Certain travertines and cave deposits of calcium carbonate, which are characterised by being banded and translucent, are the so-called onyx marbles or oriental alabasters; they are here shown (by their sp. gr.) to consist, in almost all cases, of calcite, and not of aragonite. The true onyx marbles are superficial deposits from hot springs, and, according to the view taken by the author, deposition has taken place slowly at the bottom of pools of water; cave marbles (that is, stalactites, &c.), on the other hand, are cold-water deposits, and are of greater purity. The former rarely contain less than 90 per cent. of calcium carbonate; iron oxide and carbonate being the next prominent constituents, these being the main cause of the wide range in colour. The pale and green colours are associated with ferrous carbonate, and the red-browns with ferric oxide, which latter has been produced by the oxidation of the carbonate along cracks and joints; for example, a green marble with 4.27 per cent. FeCO_3 , contained in the brown-red (oxidised) portions 1.22 per cent. FeCO_3 and 3.53 per cent. Fe_2O_3 . Some of the colour variations may be partly due to manganese; and in some amber-brown and yellow marbles (and one rose coloured) they are due to organic matter; they are rarely due to mechanical enclosures, such as clay.

Of the 16 analyses given, I is a white onyx marble, from Lower California; II, milk-white from Persia, also with 0.24 $\text{Ca}_3(\text{PO}_4)_2$; III, light green, from Mexico; IV, red-brown, from Arizona; V, dark amber, from California, containing organic matter, and 1.59 SrCO_3 and 0.11 BaCO_3 .

Sp. gr.	CaCO_3 .	MgCO_3 .	FeCO_3 .	MnCO_3 .	Fe_2O_3 .	SiO_2 .	CaSO_4 .	H_2O .	Total.
I. 2.78	96.86	0.24	2.79	—	0.61	0.06	—	not det.	100.56
II. 2.75	90.93	0.75	1.37	4.34	—	—	2.30	—	99.93
III. 2.75	89.36	3.00	5.24	0.29	—	—	1.34	0.57	99.80
IV. 2.67	93.82	0.53	4.06	—	1.73	0.05	—	not det.	100.19
V. 2.70	95.48	2.20	—	—	—	—	—	0.37	99.75

These marbles are holocrystalline; sometimes granular, but more

often fibrous or radially columnar in structure. The specific gravity varies from 2·64 to 2·79, and the hardness from 3 to 3·5; only in one case was the sp. gr. as high as 2·87 with $H = 4$, this being the only aragonite in the whole series examined. L. J. S.

Hislopite. By THOMAS H. HOLLAND (*Records Geol. Survey, India*, 1893, 26, 166—171).—Calcite from the Deccan traps, containing patches of botryoidal “green earth,” and small, bright crystals of henlandite, gave, on analysis,

Moisture.	Insoluble in acetic acid.	$Fe_2O_3 + Al_2O_3$.	CaO.	CO_2 .	Total.	Sp. gr.
4·03	23·48	0·25	40·48	30·98	99·22	2·546

The iron, aluminium, and a little calcium are due to the slight solubility of the enclosures in the acid. A specimen from Nagpur, of sp. gr. 2·659, contained 4·615 per cent. of moisture and enclosures. The calcite varies from clear and colourless to green and opaque, owing to the unequal distribution of the enclosures; and the sp. gr. decreases as the amount of the enclosures increases. The “green earth” has a sp. gr. of 2·62; it is of indefinite composition, and possibly consists of glauconite and celadonite. L. J. S.

Alteration of Diabase and Granite. Formation of Clay.

By PHILIP HOLLAND and EDMUND DICKSON (*Proc. Liverpool Geol. Soc.*, 1893, 7, 108—117).—I, Analysis of the fresh rock of a diabase dyke in the granite, at St. Helier, Jersey; II, the brown, ochreous, clayey matter into which I is weathered. III, unaltered granite from the same locality; IV, the weathered, friable rock; V, clay derived from the same.

	I.	II.	III.	IV.	V.
SiO_2	43·56	44·93	70·23	71·22	48·44
TiO_2	1·03	1·34	14·73	14·92	27·24
Al_2O_3	14·58	16·27			
Fe_2O_3	3·84	13·37	2·37	2·36	5·04
FeO	7·00	—	0·98	0·07	—
MnO	0·39	0·28	0·18	0·20	0·38
CaO	10·78	1·84	0·94	0·44	0·38
MgO	9·95	6·40	0·50	0·68	2·93
K_2O	1·02	0·84	5·13	4·10	7·43
Na_2O	1·86	2·03	4·19	4·25	0·35
CO_2	1·93	—	—	—	—
H_2O	3·85	12·55	0·70	2·10	7·91
	99·79	99·85	99·95	100·34	100·10
Sp. Gr.	2·923	2·592	2·65	2·60	—

By the prolonged action of carbonic anhydride and water under pressure on such rocks, some calcium, magnesium, and iron went into solution. These alterations are discussed in connection with the formation of clay. L. J. S.

Amount of Silica and Quartz in Granites. By STANISLAUS ZALESKI (*Tsch. Min. Mitth.*, 1894, **14**, 343—359).—The percentages of silica and quartz (the latter being separated by means of a heavy solution) of various granites are given as

	SiO ₂ .	Quartz.	
Nigg (Kincardine)	69·84	13·0	65·33
Baveno (Italy)	74·44	56·4	41·38
Dannemore (Sweden)	61·06	15·2	54·08
Hangö (Finland)	71·42	29·5	59·46

The third column gives the calculated silica percentage of the rock after deducting the quartz, and as these figures differ considerably from the silica percentage of syenite (which has 58—60), it is considered that granite is not syenite *plus* quartz. L. J. S.

Fuller's Earth from Wingen, N.S.W. By GEORGE W. CARD (*Records Geol. Survey, N.S.W.*, 1894, **4**, 30—32).—A yellowish-green, unctuous clay from this locality gave the following analysis, by Mingaye. Under water, it softens and disintegrates; when heated, it becomes colourless, finally fusing to a green glass.

H ₂ O (moisture).	H ₂ O (com- bined).	SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	CaO.	MgO.	K ₂ O.	Na ₂ O.	Total.
13·73	6·45	50·61	19·35	3·55	1·37	3·24	0·92	0·47	99·69

There is a trace of P₂O₅; FeO, MnO, and SO₃ are absent.

L. J. S.

Physiological Chemistry.

Metabolism Experiment on Sheep with a Pettenkofer Respiration Apparatus. By FRANZ LEHMANN (*Exper. Stat. Record*, 1895, **7**, 235—236; from *Landw. Jahrb.*, 1895, **24**, Suppl. 1, 117—119).—Protein, fat, starch, and cellulose were compared as producers of fat and lean meat respectively. Two sheep were fed with a ration rather more than sufficient for maintenance. After the production of lean and fat had been determined, the constituents to be tested were added in separate periods, between each of which the basal ration intervened. The amounts given in each period were as follows (in grams).

	Protein.	Fat.	Crude fibre.	N-free extract.
1. Basal	96·9	15·2	84·7	287·7
2. Starch	98·2	15·1	89·8	369·0
3. Cellulose ..	100·2	16·7	156·8	320·3
4. Protein	178·5	16·0	88·5	312·7
5. Fat	103·0	49·7	86·2	295·0

The basal ration resulted in a very slight production of lean meat

and much fat. The addition of starch and cellulose gave rise (equally) to a considerable increase in lean, but cellulose was much inferior to starch in fat production. The addition of protein produced the greatest increase in lean, whilst fat produced fat alone, being without effect on the production of lean.

N. H. J. M.

Normal Occurrence of Iodine in the Body. By EUGEN BAUMANN (*Zeit. physiol. Chem.*, 1895, **21**, 319—330).—In the course of investigations on the active physiological substance of the thyroid gland, a substance was obtained, to which the name *thyroidin* is applied. The glands, when boiled for some days with 10 per cent. sulphuric acid, yield a liquid which deposits a flocculent precipitate; this, after extraction with alcohol, is regarded as the active substance. It may be a derivative of nucleic acid: it contains 0.54 per cent. of phosphorus, but it cannot be obtained from the thymus gland, nor from pure nucleic acid; the most remarkable point about it is that it contains iodine in organic union in considerable amount.

W. D. H.

A Dermoid Cyst. By VICTOR LIEBLEIN (*Zeit. physiol. Chem.*, 1895, **21**, 285—287).—The contents of an ovarian cyst of dermoid nature contained 83—87 per cent. of water. The quantity of ethereal extract was large, and it contained cholesterol; ischolesterol and cetylic alcohol were not detected, although the latter is stated to have been found in a dermoid cyst by Sotnitschewsky, *ibid.*, 1880, **4**, 345.

W. D. H.

A rapid Method of Desiccating and Sterilising Serum. By CHARLES JAMES MARTIN (*J. Pathol. and Bacteriol.*, 1896, **3**, 507—509).—The simple apparatus used is figured. The method consists essentially in filtering the serum through a Pasteur-Chamberland filter into a bottle connected with a water pump; the whole is kept at 40°, and the serum, which comes through in bubbles, dries as quickly as it filters.

W. D. H.

Excretion of Oxalic acid. By JAMES CRAUFURD DUNLOP (*J. Pathol. and Bacteriol.*, 1896, **3**, 389—429).—Oxalic acid is a constant constituent of the urine of men eating ordinary diet; in the urine, excess of calcium salts tends to precipitate the acid, but in normal urine this is prevented by acid sodium phosphate, and possibly by other substances. The precipitation is most liable to occur if the percentage of oxalic acid in the urine is high, and, in fact, actually occurs in about one in every three specimens; the precipitated calcium oxalate is in the form of octahedra. The daily excretion of oxalic acid averages 0.017 gram.

Alcohol is an efficient precipitant of the oxalate, and may be used in both qualitative and quantitative analysis. Oxalic acid is not a product of metabolism, but is absorbed directly from the food, and is excreted as such; increased acidity of the gastric contents aids absorption. Oxaluria is not a special morbid condition, but is essentially a hyperacid dyspepsia.

W. D. H.

Experimental Anæmia in Dogs. By RALPH STOCKMAN (*J. Pathol. and Bacteriol.*, 1896, **3**, 385—388).—In one dog, anæmia was produced by bleeding; in another, by giving food containing insufficient iron. Both factors are probably concerned in actual chlorosis, as, in both dogs, examination of the blood from day to day, and of the organs after death, show many similarities to that disease. The animals, however, possess a power of regenerating the corpuscles, a power which in chlorosis is extremely limited by some superadded condition. W. D. H.

Acetonuria. By JOHN HILL ABRAM (*J. Pathol. and Bacteriol.*, 1896, **3**, 430—432).—The present experiments confirm Becker's (*Deut. med. Woch.*, 1895, No. 19) original statement that acetonuria follows anæsthesia in two-thirds of the cases, the anæsthetic used making no difference; if acetonuria is present before, anæsthesia increases it. The probable source of acetone is proteid destruction. The practical outcome is that, except in cases of urgency, anæsthetics should not be administered to diabetic patients. W. D. H.

Hæmatoporphyrinuria. By ARCHIBALD E. GARROD and F. GOWLAND HOPKINS (*J. Pathol. and Bacteriol.*, 1896, **3**, 434—448).—Normal urine contains a little hæmatoporphyrin, but the amount is considerably increased by various conditions, especially by taking sulphonal. Three such cases are recorded in the present paper, which gives a clinical history of each case with chemical and spectroscopic examinations of the blood and urine. The causation of this condition is not yet fully explained, and the principal new point that comes out in the present research is that urinary hæmatoporphyrin does not imply excessive blood destruction; there is, at any rate, no corresponding increased excretion of iron. The best way to obtain the pigment from the urine is to add sodium hydroxide, and then extract the pigment from the washed precipitate of phosphates, or to saturate the urine with ammonium chloride, and extract the pigment from the urates with a mineral acid. W. D. H.

Poisoning of Cattle by Potassium Nitrate. By N. S. MAYO (*Exper. Stat. Record*, 1895, **7**, 250; from *Kansas Stat. Bull.*, No. 49, 3—11).—A number of cattle fed on dried cornstalks having died, the stalks were examined and were found to contain, both outside and inside, a quantity of potassium nitrate. The corn had grown on very rich soil formerly used as a hog lot. In direct experiments with potassium nitrate on animals, a heifer (about 500 lbs.) drenched with a solution of nitrate (300 grams) died within 24 hours; a cow (1,200 lbs.) was killed by 500 grams, and an adult rabbit by 5 grams of potassium nitrate. The symptoms are described in the original paper. N. H. J. M.

Poisonous Effects of Acetylene. By L. BROCIER (*Compt. rend.*, 1895, **121**, 773—774).—Experiments previously made by the author (*Annales d'Hygiène*, 1887, [3], **17**, 454) show that 100 vols. of blood dissolve about 80 vols. of acetylene; the solution shows no characteristic spectrum, and is reduced by ammonium hydrosulphide as readily

as ordinary arterial blood. In a vacuum, part of the acetylene is evolved at the ordinary temperature and part at 60° . If the blood is allowed to putrefy, the volume of acetylene given off at the ordinary temperature remains practically the same, but the quantity liberated at 60° decreases as putrefaction advances. If any compound of acetylene and hæmoglobin is formed, it is very unstable, and is not analogous to carboxyhæmoglobin. The poisonous action of acetylene is very feeble, and animals can breathe large quantities of the gas for several hours without injurious effect, provided the proportion of oxygen is kept up to the normal amount, and the products of respiration are not allowed to accumulate (compare this vol., ii, 200).

C. H. B.

Chemistry of Vegetable Physiology and Agriculture.

Growth of Cholera Bacilli in Sunlight. By F. F. WESBROOK (*J. Pathol. and Bacteriol.*, 1896, **3**, 352—358).—Direct sunlight destroys cholera bacilli if they are in contact with air, but aids by its heating power the growth of those not in free contact with air.

W. D. H.

Origin of Atmospheric Oxygen. By THOMAS L. PHIPSON (*Compt. rend.*, 1895, **121**, 719—721).—Plants such as *Convolvulus arvensis*, grow readily in an atmosphere of moist nitrogen containing a certain quantity of carbonic anhydride, and eventually the atmosphere may contain more oxygen than is present in the air. The lower plants, such as *Protococcus*, *Conferva*, *Ulva*, &c., behave similarly, and, for a given weight, liberate much more oxygen in a given time than plants of higher organisation. These facts support the author's view that originally the earth's atmosphere consisted mainly of nitrogen, together with some carbonic anhydride, and that the presence of oxygen is due to the decomposition of the carbonic anhydride by plants. They also indicate that plants are essentially anaërobic, although the gradual increase in the proportion of oxygen in the air may have led to the gradual modification of the anaërobic cells and their conversion into aërobic cells like those of fungi.

C. H. B.

Metabolism and Respiration of Sprouting Potato Tubers. By E. ZIEGENBEIN (*Bied. Centr.*, 1895, **24**, 784; from *D. Landwirt*, 1895, No. 32).—Observations made with sprouts of *Lupinus luteus* showed that the albumin decomposes at about the same rate in absence, as in presence of oxygen. Free nitrogen was not evolved during 24 hours. The conditions of light only essentially influence the decomposition of proteïds, so far as light increases the production of carbonic anhydride in sprouting potato tubers, but hinders the growth of the shoots. The temperature optimum for the normal respiration of *Taraxacum officinalis* is 40° (the same as that found by Clausen for *Triticum*, *Lupinus*, and *Syringa* flowers), for sprouts of *Abies excelsa*,

and seedlings of *Vicia faba* 35°, and for potato tubers 45°. Above these temperatures, the energy of respiration diminishes slowly until the maximum is reached (about 10° higher than the optimum), but very rapidly at still higher temperatures. N. H. J. M.

Assimilation of Lecithin by Plants. By JULIUS STOKLASA (*Sitzungsber. k. Akad. Wissens. Wien.*, 1895, 104; Abth. I, 1—11).—Lecithin occurs in soil in quantities varying with the amount of organic matter. This and the importance of lecithin in the production of chlorophyll lend interest to the question of its assimilation by plants.

Water-culture experiments were made in which oat sprouts were grown in nutritive solutions (1) free from phosphorus, (2) containing calcium phosphate, and (3) containing lecithin. In the case of lecithin, the solution had to be frequently changed owing to the decomposition of the lecithin into glycerol phosphate, choline, and fatty acids. The plants grew best in presence of calcium phosphate. In the lecithin cultures, the nutrition was not sufficient, but the lecithin was no doubt assimilated. Without phosphorus, the plants produced no seed, and ceased growing after 96 days. The following table shows the average amounts of dry produce, the total phosphoric acid and the lecithin in the produce grown in solutions containing (1) calcium phosphate, (2) lecithin, and (3) no phosphorus.

	Dry produce.				P ₂ O ₅ .	Lecithin.
	Roots.	Stems, &c.	Grain.	Total.		
1 ..	3·95	18·47	7·45	29·87	0·110	0·120
2 ..	2·15	14·10	4·27	20·52	0·0605	0·0882
3 ..	0·68	1·41	—	2·09	0·0037	—

The results of the experiments show clearly the assimilation and utilisation of lecithin by the oats. Assimilation of phosphorus in an organic form by plants had not been proved before.

N. H. J. M.

Effects of Chlorides, Bromides, and Fluorides on Algæ. By M. WYPLEL [? WYPFEL] (*Bied. Centr.*, 1895, 24, 785; from *Bot. Centr.*, 1895, 62, 216; compare *Abstr.*, 1895, ii, 175).—Different Algæ vary in their power of resisting the action of solutions of salts, the higher Algæ being more sensitive than the lower. *Spirogyra* is the most sensitive, then *Edogonium* *Vaucheria*, *Stichococcus*, *Oscillaria*, *Pleurococcus*, and *Protococcus* in the order given. As regards chlorides, the ammonium salt is the most injurious, then manganese, aluminium, and barium chlorides. Even *Protococcus* dies in 2—4 per cent. solutions of these salts. Magnesium chloride is the least injurious; the sodium and strontium salts are less active than potassium chloride. Of bromides, the ammonium salt is again the most injurious, then potassium and sodium salts. Sodium, potassium, and ammonium fluorides are injurious even in 1/8th per cent. solutions.

Sodium and calcium nitrates are more favourable to Algæ than potassium nitrate. The effect of the chlorides, &c., is to retard growth and hinder division of cells. The amount of starch is diminished, the cell membrane thickened, and the colour of the chlorophyll changed and finally destroyed. Weak solutions are injurious after prolonged contact. N. H. J. M.

Effect of Copper Salts on the Growth of the Vine and on Soil. By BERLESE and LIVIO SOSTEGNI (*Bied. Centr.*, 1895, **24**, 768—769; from *Bot. Centr.*, 1895, **63**, 270).—When copper bicarbonate is added to a nutritive solution in which vines are growing, the copper is taken up in traces by the roots. Vine leaves are more sensitive to soluble copper salts than the *Peronospora* mycelium, and the leaf is only protected from *Peronospora* as long as soluble copper compounds are present on the surface. The mycelium will develop on portions of leaves not reached by the copper solutions. When the roots of a vine were allowed to grow in 1 per cent. aqueous copper sulphate, copper could only be detected in the roots. In the case of branches immersed in copper sulphate solution, only the walls of the fibrovascular bundles were attacked at first, after which the solution penetrated further mechanically. Contrary to Millardet, it was found that only the collenchyma, and never the cuticula, took up copper.

In the absorption of copper sulphate by soil, lime takes the predominant part, alkalis, magnesia, iron, and alumina being dissolved. Humic acid and silicates do not combine with copper. The copper remains in the soil as oxyhydrate of the basic sulphate, or as a double salt of copper and calcium. The basic sulphate being readily decomposed by carbonic anhydride, dissolves, and is absorbed by plants.

N. H. J. M.

Injurious Action of Cobalt and of Barium on Plants. By EMIL HASELHOFF (*Landw. Jahrb.*, 1895, **24**, 959—961; 962—967).—By means of water-culture experiments, it was shown that, like nickel (Abstr., 1894, ii, 208), cobalt is injurious to vegetation; 1 to 2 parts per million being sufficient to destroy the plants.

As regards barium, experiments with maize and with beans showed that very small amounts injure vegetation. The ashes of plants so treated contained small amounts of baryta. It is possible that increased application of lime would, to some extent, hinder the taking up of baryta by the plant.

N. H. J. M.

Pectase. By GABRIEL BERTRAND and ALFRED MALLÉVRE (*Compt. rend.*, 1895, **121**, 726—728).—Pectase is of very common occurrence in plants (compare Abstr., 1895, i, 312), and was found by the authors in 40 species of plants containing chlorophyll, five of which belonged to the cryptogams. It is found in the roots, stems, leaves, flowers, and fruit. The time required for the plant juice to coagulate a 2 per cent. solution of pectin varies from less than a minute, in the case of potatoes, clover, lucern, and others, to two hours in the case of carrots, and 48 hours in the case of ripe tomatoes. The activity of the ferment varies not only with different plants, but also with

different organs of the same plant, and as a rule is most abundant in the leaves, and especially the leaves of rapidly growing plants.

It can be prepared from the leaves of lucern or clover in vigorous growth; these are bruised and pressed, and the juice is saturated with chloroform and allowed to remain for 24 hours in a well-closed flask in the dark. It is then filtered, the limpid filtrate mixed with twice its volume of alcohol of 90°, and the white precipitate thus formed is suspended in a small quantity of water. After 12 hours, it is filtered, and the filtrate allowed to run into a large excess of alcohol; the precipitated pectase, when dried in a vacuum, forms a white, non-hygroscopic solid, very soluble in water. C. H. B.

Laccase in Fungi. By EMILE E. BOURQUELOT and GABRIEL BERTRAND (*Compt. rend.*, 1895, 121, 783—786).—Examination of 200 different species of fungi belonging to different genera shows that the great majority contain laccase, and in certain cases the presence of laccase coincides with the existence of a distinct odour, and in others with the existence of constituents that become coloured when exposed to air. Whilst in some genera or sub-genera such as *Russula*, *Lactarius*, and *Psalliota*, almost all the species contain laccase; in others, such as *Marasmius*, *Hygrophorus*, *Cortinarius*, and *Amanita*, few or none contain the ferment. Further, the proportion of laccase varies in different parts of the same plant, and may be absent in the young plant, but present at a later stage of development (compare Abstr., 1895, i, 386). C. H. B.

Amount of Substances soluble in Water in Plants. By E. GAIN (*Exper. Stat. Record*, 1895, 7, 187—188; from *Bull. Soc. Bot., France*, 1895, 41, 53—67).—The amounts of soluble matter in plants grown in dry and in wet soil were determined by macerating the powdered substances with hot water and determining the dry matter in the extracts. The results show that plants grown in wet soils contain more soluble matter than when grown in dry soils, and that the parts of the plant above-ground contain more soluble matter than the roots. In comparing analyses of most plants, it is very important to consider the different conditions under which they were grown. N. H. J. M.

Sulla (*Heydoarum coronarium*). By L. GRANDEAU (*Exper. Stat. Record*, 1895, 7, 206—207; from *J. Agr. Prat.*, 1895, 59, 812—814 and 850—854).—Perennial, white sulla is considered suitable for meadows on thin, poor, dry soils, and is said to thrive, even on pure schists. There are also a native Algerian biennial variety, and a red variety. The stems and leaves of red sulla were analysed with the following results (per cent. in fresh substance).

Water.	Proteid.	Fibre.	N-free extract.	Fat.	Ash.	P ₂ O ₅ .	K ₂ O.
85·00	2·38	4·63	5·75	0·27	1·97	0·117	0·116

The fresh roots had the following percentage composition.

Water.	Organic matter.	N.	Ash.	K ₂ O.	CaO.	MgO.	P ₂ O ₅ .
78·50	19·49	0·22	2·01	0·10	0·32	0·11	0·06

The plant withdraws less potash from the soil (72 lbs. per acre) than most other leguminous plants. Owing to the immense quantity of nitrogen in the crop (224 lbs. per acre), presumably obtained largely from the air, sulla seems well suited as a crop for green manuring on land not irrigated in semi-arid regions.

The nutritive value is about the same as that of red clover.

N. H. J. M.

Importance of Potash as Plant Food. By C. VON FEILITZEN (*Bied. Centr.*, 1895, **24**, 732—733; from *Svensk. Mosskult.-förening. tidskr.*, 1894, 283—287; 1895, 211—214).—In a number of zinc cylinders filled with peaty soil, well limed in 1888 and 1892, and yearly manured with (2) basic slag alone, (3) kainite and (4) felspar, respectively, oats, clover (two years), rye, and peas were successively grown; there was also a short experiment (1) without manure. Oats and rye had, in addition, a dressing of sodium nitrate. The following amounts of produce were obtained (in grams).

	Oats.		Clover (green).		Rye.		Peas.	
	Straw.	Grain.	1890.	1891.	Straw.	Grain.	Straw.	Grain.
1....	25·3	7·4	0	3·0	16·0	2·0	23·5	7·0
2....	115·6	56·3	318	71·0	52·0	19·0	102·5	63·7
3....	123·8	62·2	589	70·3	98·6	40·0	120·0	100·0
4....	112·6	54·6	349	97·4	54·6	20·3	92·8	58·2

The importance of potash for peaty soils was also shown by the results of field experiments in various parts of Sweden. Both insufficient and excessive potash manuring should be avoided, as potash is not so readily absorbed by the soil as phosphoric acid. Thus, the drainage from the peaty soils of Jönköping generally contain 0·3—0·5 gram (on one occasion 1·2 gram) of potash per hectolitre; 2—26 grams of lime; only traces of phosphoric acid.

N. H. J. M.

Application of Phosphates and Superphosphates to Acid Soils. By G. PAGEOT (*Bied. Centr.*, 1895, **24**, 743—744; and by L. GRANDEAU (*ibid.*, 744); from *Jour. Agric. Prat.*, 1895, **2**, 334—337 and 337—338 respectively).—Pageot found that the soil contained P_2O_5 0·035, K_2O 0·042, Na_2O 0·060, CaO 0·879, MgO 0·110, SO_3 0·068, and N 0·193 per cent. Whilst basic slag and crude phosphate had no appreciable effect, superphosphate converted the worthless, sterile soil in three years into a fertile arable soil which yielded 30 to 35 hectolitres of wheat per hectare.

Grandeau suggests that the favourable effect of superphosphate compared with the other phosphates may be due to the sulphuric acid it contains. Sulphur in an assimilable form is essential, and nothing is known as to the availability of the sulphate in the soil in question.

N. H. J. M.

Investigations [on Manures] at Halle. By MAX MÄRCKER (*Bied. Centr.*, 1895, **24**, 734—743; from *Ber. Versuchs-Stat. Halle a. S.*, 1895,

49 pp.).—*Application of Crude Potassium Salts to Beetroot.*—Whilst in extremely wet or dry seasons the application of potash has no certain quantitative effect, in moderately dry years the effect will always be considerable. It is only in very special cases that potash can act injuriously on the production of sugar.

Experiments on Manuring Beetroot with Potassium and Sodium Nitrates.—Experiments were made in order to decide whether it is the nitrogen of sodium nitrate, or the soda which causes diminished sugar production in beetroot. The results showed that with small applications of sodium and potassium nitrates respectively, the roots manured with potassium nitrate contained rather less sugar than those manured with sodium nitrate, and that with large applications there was slight diminution in the amount of sugar in both potash and soda plants; so that sugar production may be diminished by potassium as well as by sodium nitrate.

Experiments with Phosphates.—Potassium metaphosphate, a product of the Stassfurt industry, containing 53·6 per cent. of phosphoric acid, gave good results with barley; it is probably rapidly changed into orthophosphoric acid, either in the soil or in the plant. The phosphates of the sludge of sugar works gave very poor results with a first crop, owing to the amount of free lime present; with a second crop, however, very good results were obtained, and it is thought that a heavy dressing would render phosphate manuring unnecessary for two years. Bone meal, as compared with bone superphosphate, has comparatively little effect in the second year. As a nitrogenous manure bone meal may give, according to the conditions, very good results. As regards basic slag, the best results are obtained with products rich in citrate-soluble phosphates, not only with the first but with subsequent crops.

Stable Manure and its Constituents.—The effect of sodium nitrate was compared with (1) urine, (2) fæces, (3) mixture of fæces and urine, and (4) stable manure. The nitrogen of urine gave very satisfactory results, an average of 89·2 per cent. of the effect of the nitrogen as sodium nitrate. The nitrogen of fæces gave only a very slight increase of produce, about 11 per cent. of the effect of an equal amount of nitric nitrogen. The effect of the mixture of fæces and urine was about the same as when used singly, whilst stable manure showed an average effect of 34·25 per cent. of an equal amount of nitric nitrogen.

As regards losses of nitrogen in animal excrement, the results of experiments showed that whilst fæces and urine lost over half the total nitrogen (in five months), the addition of peat litter alone reduced the loss to 20·11 per cent. With a small quantity of phosphoric acid (as well as peat litter), the loss was 21·78 per cent.; with four times the amount of phosphoric acid, 7·82 per cent.; with small and larger amounts of sulphuric acid (2 and 4 per cent. of the dry matter of the peat), the losses were 5·68 and 5·64 per cent.; whilst with lime (10 per cent. added to the peat) 16·5 per cent. of the total nitrogen was lost. The best of the mixtures is therefore peat and sulphuric acid (2 per cent.). Nitrification was most active under the influence of lime, 29·82 of the total nitrogen being nitrified in the five months

of the experiment (28·76 in the first two months). The next largest amount of nitric nitrogen was produced under the influence of the greater amount of phosphoric acid, namely, in five months, 22·11, and in two months 4·08 per cent. of the total. With sulphuric acid (4 per cent.), there was, after five months, only 1·52 per cent. of the total nitrogen in the form of nitric acid; whilst with 2 per cent., 16·41 per cent. of the nitrogen was nitrified. In the original substance alone, 3·37 per cent. of the nitrogen was nitrified; with the addition of peat, 19·49 per cent. was nitrified. In the original paper, the percentage amounts of albuminoid, ammonia, nitric and amide nitrogen in the original mixtures, and, after two and five months respectively, are given in a table.

Effect of Kainite and Carnallite on the yield and composition of Grass.—By potash manuring, the vegetation of meadows becomes less nitrogenous, although the total nitrogen is greater. With carnallite, at least as much nitrogen was taken up as when kainite was employed. Under the influence of potash, the first crop is rendered distinctly poorer in phosphates, whilst the second crop is much richer than without potash manure. The first cutting of grass manured with potash is much richer, and the second crop poorer, in potash than when no potash is applied.

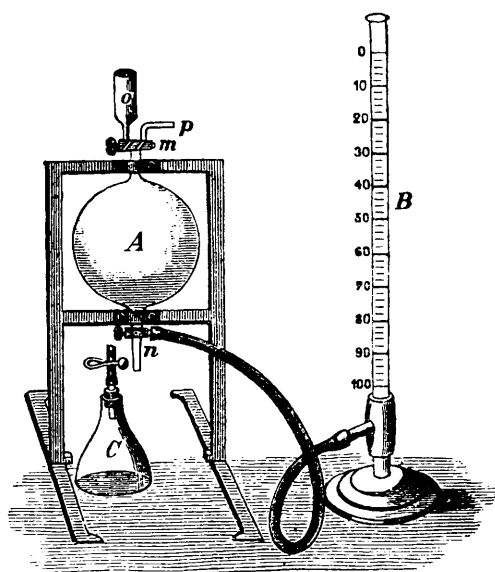
N. H. J. M.

Analytical Chemistry.

Apparatus for Gas Analysis. By OTTO BLEIER (*Ber.*, 1896, **29**, 260—265; compare this vol., i, 70).—The author describes a form of the Orsat-Muenke apparatus modified in accordance with the principles laid down in his previous paper. The measuring tube is connected below with a three-way cock, so that the water can be slowly run out, and be replaced by the gas to be analysed. A two-way cock is attached to the top of the measuring tube, and serves to connect the tube with the pipettes, or with the vessel from which the sample of gas is to be taken. The first two absorption pipettes are also fitted with three-way cocks. The advantages of the apparatus are that time is saved by the automatic measurement of the gas, and that the solubility of the gas in water introduces no error.

An apparatus is also described which can be used for gas titration, or for complete gas analysis. The glass bulb A (see Fig., next page), of 500—600 c.c. capacity, has attached to its upper end a two-way cock, and to its lower a three-way cock, which is attached by india-rubber tubing to the measuring tube B. An exhausted flask, C, can also be attached to the three-way cock by means of the tube *n*, which also serves to empty the bulb of any liquid. For a gas titration, the bulb is first dried, and then the gas is introduced, either through *p* or *n*, according as it is heavier or lighter than air, and is allowed to pass through for a short time till all the air is displaced; it is then measured at atmospheric temperature and pressure. If it is not necessary to measure

the absorbent liquid (for example, water for ammonia or hydrogen chloride, sodium hydrogen carbonate for sulphurous anhydride), it is



run in from the cup O, and finally run out through *n* into the exhausted flask, the bulb is washed out with water, and the washings are also run into the flask. The contents of C are then titrated in the usual way. If it is necessary to measure the amount of absorbing liquid used, this is accomplished in B, care being taken to remove all the air in the rubber tube by allowing a small quantity of the liquid to flow out through *n*. If the apparatus is to be used for absorption analysis, the gas is measured

by the replacement of water in the bulb, the absorbing liquid is placed in B, and the absorption is then measured by diminution of liquid in B. After one absorption, the liquid can be removed, the measuring tube washed out, and then filled with the second absorbent.

J. J. S.

Apparatus for Quantitative Electrolysis. By MAX GRÖGER (*Zeit. angew. Chem.*, 1895, 625—626).—The apparatus consists of a battery glass 80 mm. wide, 30 mm. broad, and 120 mm. high, through one short side of which passes a horizontal platinum wire, 1 mm. thick, and 70 mm. long, from which is suspended the cathode. This consists of a carefully weighed square of platinum foil (12 grams in weight) reaching nearly to the bottom of the glass. On the opposite side to the long wire is fixed a short, bent wire, from which is suspended the anode, which consists of a 1 mm. thick, looped platinum wire, weighing about 16 grams: this is first bent rectangularly, the ends being finally twice bent upwards and downwards so as to form a series of loops on each side of the cathode. The galvanic current is admitted from the outside through connecting pieces attached to these wires. During the electrolysis, the glass is covered, to prevent loss by spirting, the cover being occasionally rinsed. The principal advantage of the apparatus is the cheapness of the electrodes.

L. DE K.

Estimation of Water in Silicates. By PAUL JANNASCH and P. WEINGARTEN (*Zeit. anorg. Chem.*, 1895, 11, 37—39; compare Abstr.,

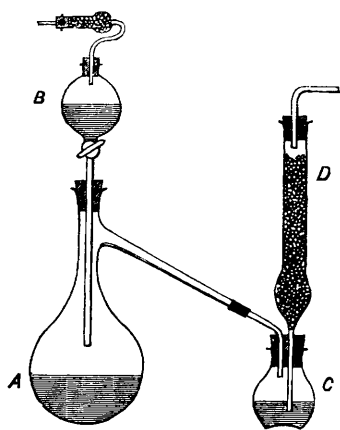
1895, ii, 325).—The authors have modified their process of estimating the water in silicates by heating them, mixed with dry borax, in a current of dry air, so that the sample employed may be used for the estimation of other constituents. The method is identical with that previously described, except that the mixture of silicate and borax is heated in a platinum boat; it is essential that the mixing be very thorough. E. C. R.

Citrate Method of determining Phosphoric acid. By F. BERGAMI (*Exper. Stat. Record*, 1895, 7, 180—181; from *Journ. Franklin Inst.*, 1895, 140, 139—152).—The method, which is especially for insoluble phosphates, is as follows. The substance (2 grams) is boiled with a mixture of strong nitric (40 c.c.) and hydrochloric acids (10 c.c.), diluted to 250 c.c., and aliquot parts of the solution, corresponding with 0.2 and 0.4 gram of substance, are mixed with 20, 50, 75, and 100 c.c. respectively of Märcker's citrate solution, prepared by dissolving citric acid (250 grams) in water, adding 24 per cent. ammonia (500 c.c.), and diluting with water to 1500 c.c. 25 c.c. of official magnesia mixture is then added, the whole well stirred for half an hour, and the precipitate treated as usual.

The results depend largely on the amount of citrate solution employed. With high grade phosphates (20 to 30 per cent.), the best results are obtained by using 50 to 75 c.c. of citrate solution for 0.2 gram of substance, or 75 c.c. to 100 c.c. for 0.4 gram. Slightly lower results were obtained than with the molybdate method, probably owing to an excess of citrate. N. H. J. M.

Rapid Estimation of Insoluble Phosphate. By VINCENT EDWARDS (*Chem. News*, 1896, 73, 25).—Although not advocating the substitution of a volumetric for the gravimetric method of estimating insoluble phosphate, yet the following method is submitted as satisfactory. The residue, from the exhaustion of 0.5 gram of the substance with cold and hot water, is boiled for a short time in water containing a very small quantity of hydrochloric acid, filtered, made up to 300 c.c., rendered alkaline with ammonia, and then faintly acidified with acetic acid. The solution is then placed on a sand bath and titrated hot with standard uranium acetate of the strength 1 c.c. = 0.01 gram $\text{Ca}_3\text{P}_2\text{O}_8$. D. A. L.

Testing for Arsenic in Alloys of Tin and Lead. By LEONARD DE KONINGH (*Ned. Tydschr. Pharm.*, 1895, 7, 330—331).—The alloy is distilled with hydrochloric acid and ferric chloride in a small retort, connected with a large Peligot tube containing a little water. It is advisable to apply but a very gentle heat at first, so that the solution may take place at the expense of the chlorine of the ferric chloride; the evolution of hydrogen is then hardly noticeable, and the formation of arsenic hydride is reduced to a minimum. Finally, the liquid is distilled nearly to dryness; the arsenic in the distillate may be at once precipitated by hydrogen sulphide. L. DE K.



Apparatus for the Estimation of Sulphur in Iron. By E. J. READ (*Chem. News*, 1895, **72**, 299).

—The end of the tube D is adjusted in the flask C, so that some of the absorbing liquid is forced up among the beads by the passage of the gas, evolved from the sample in the flask A, by the action of the acid from B. The apparatus is preferably used under reduced pressure.

D. A. L.

Estimation of Sulphur and Carbon in Zinc. By ROBERT FUNK (*Zeit. anorg. Chem.*, 1895, ii, 49—58; compare this vol., ii, 247).—The sulphur is estimated as follows.

About 20 grams of the zinc is dissolved in pure hydrochloric acid, and the gas evolved passed through a Pettenkofer's tube (50 cm. long), containing a mixture of equal volumes of a solution of zinc sulphate (2 per cent.) and ammonia (0.5 per cent.). The contents of the tube are transferred to a glass cylinder, acidified with hydrochloric acid, and mixed with 1 c.c. of a solution of paramidodimethylaniline in hydrochloric acid (1 : 500), and a few drops of a solution of ferric chloride (10 per cent.). If sulphur is present, a coloration of methylene-blue is produced, and this is compared with the colour produced by a known quantity of hydrogen sulphide. In order to remove any sulphurous acid or hydrogen sulphide which may be present, the hydrochloric acid employed must first be boiled with a small quantity of potassium chlorate, and the excess of chlorine removed with pure zinc or alcohol. Various samples of purified zinc, when examined by this method, were found to contain from 0 to 2.5 parts of sulphur in 10,000,000 parts of zinc.

The carbon is determined by burning the zinc with copper oxide. A combustion tube, closed at one end, is charged with a column, 8 cm. long, of freshly fused potassium chlorate, then with a column of granular copper oxide, followed by the zinc in a porcelain boat, and another column of copper oxide. The tube is exhausted by means of a mercury pump, and after the front column of copper oxide has been heated to redness, the zinc is volatilised. When the zinc is entirely volatilised, the potassium chlorate is cautiously heated; the evolved oxygen is at first entirely absorbed by the metals; when this absorption ceases, which is indicated by a mercury manometer, and the pressure in the tube reaches that of the atmosphere, the gas is allowed to pass through a Pettenkofer's tube, containing a solution of barium hydroxide or basic lead acetate. The sample of zinc to be tested is first washed with hydrochloric acid, and then dried in a current of hydrogen.

By the above methods 1 part of sulphur in 10,000,000 parts of zinc and 1 part of carbon in 100,000 parts can be detected. The purified

zinc of commerce contains distinct traces of sulphur and minute traces of carbon. These impurities are not soluble in the metallic zinc, and can be completely separated by filtration through asbestos.

E. C. R.

Estimation of Sulphurous Anhydride in Carbolie Powders.

By LEONARD DE KONINGH (*Ned. Tydschr. Pharm.*, 1895, **7**, 329—330).—Ten grams of the sample is distilled with hydrochloric acid, and the distillate is condensed in a large Peligot tube containing a little water and a sufficiency of bromine. The distillation is continued until the bromine has been nearly decolorised by the action of the phenol or cresol vapours. After filtering, the liquid is precipitated by barium chloride, and the precipitate calculated into sulphurous acid.

When testing carbolie powders, it must be remembered that the greater part of the sulphurous acid may have been lost either through evaporation or oxidation.

L. DE K.

Separation of Quartz from other varieties of Silica.

By GEORG LUNGE (*Zeit. angew. Chem.*, 1895, 593; 689—690).—A reply to Michaelis stating that aqueous soda decidedly attacks quartz, and that in any case it is much the same thing from an analyst's point of view whether the finely divided quartz is lost by actual solution or by mechanically passing through the filter.

The author still prefers using sodium carbonate.

L. DE K.

Detection and Estimation of Barium Sulphate.

By LEONARD DE KONINGH (*Ned. Tydschr. Pharm., &c.*, 1895, **7**, 257).—To test insoluble siliceous matters for admixed barium sulphate, the author recommends heating with strong sulphuric acid, which soon dissolves the barium compound, and leaves the silicate wholly, or partially, insoluble.

After decanting, or filtering through a suitable medium, the barium sulphate may be completely recovered by diluting with water. If the mixture should contain lead, recognisable by the ammonium sulphide test, this must first be removed.

L. DE K.

Volumetric Method for Lead Analysis.

By ALFRED C. BEEBE (*Chem. News*, 1896, **73**, 18).—The substance is dissolved in nitric acid, with a little hydrochloric acid, if required, evaporated with sulphuric acid until white fumes of sulphuric anhydride are evolved, diluted, cooled, an equal volume of alcohol added, and, after a short time, filtered, and washed well with hot water. The precipitate is digested, with frequent and vigorous stirring, for 15 minutes, in a cold saturated solution of ammonium carbonate, filtered, the lead carbonate washed thoroughly with hot water, dissolved in hot dilute acetic acid, cooled and titrated with a 1 per cent. solution of potassium ferrocyanide, using uranium acetate acidified with acetic acid as the indicator. In this method, barium and calcium are harmless; arsenic, iron, copper, and zinc should be eliminated in the thorough washing of the lead sulphate; whilst antimony could be removed by the use of tartaric acid in the decomposition of the substance.

D. A. L.

Estimation of Manganese and Tin by Electrolysis. By CARL ENGELS (*Ber.*, 1895, 28, 3182—3189).—Manganese peroxide is deposited in a perfectly coherent form when 10 grams of ammonium acetate and 1.5—2 grams of chrome alum are added to a solution of manganese sulphate containing 0.2—0.25 gram of manganese in 150 c.c. water. The electrolysis must be carried out in a platinum vessel with a matt surface, a current density of 0.6—1 ampère, and an electromotive force of 3—4 volts being used. The deposit is washed, ignited, again washed to remove small traces of chromium compounds, and finally heated and weighed. Alcohol and ammonium acetate also produce good and coherent deposits of manganese peroxide. The addition of a hydroxylamine salt to an acid solution of a manganese salt prevents the deposition of manganese peroxide, and thus enables several separations to be carried out.

Tin can also be readily obtained in a coherent film by electrolysis, adding to the solution hydroxylamine sulphate, together with a little ammonium acetate and tartaric acid, a current density of 0.5—1 ampère and an electromotive force of 4—6 volts being used.

The methods proposed for both manganese and tin appear to give excellent quantitative results.

A. H.

Analysis of Chrome-iron Ore, Ferrochromium, and Chrome-steel. By SAMUEL RIDEAL and SIGMUND ROSENBLUM (*Chem. News*, 1896, 73, 1—2).—The authors review the past work on, and give a bibliography of, this subject. They point out that finely powdered chrome-iron ore and ferrochromium may be decomposed by fusing with sodium peroxide, in the first case for five, in the second for ten, minutes, and in both cases allowing to cool slightly, adding more peroxide, and heating again. Before the subsequent titration, the solution should firstly be boiled for 10 minutes, then acidified, and finally filtered, if necessary.

D. A. L.

Technical Analysis of Cyanide Working Solutions. By WILLIAM BETTEL (*Chem. News*, 1895, 72, 298—299; compare this vol., ii, 224).—Simple or readily decomposable complex cyanides are not affected by dilute permanganate in an acid solution and in the absence of organic matter, but *ferrocyanides* and *thiocyanates* are rapidly oxidised. Therefore, to estimate the latter, the quantity of both is first ascertained by titrating 10 or 20 c.c. of N/100 permanganate, strongly acidified with sulphuric acid, with the cyanide solution; then the proportion of thiocyanate is determined by removing the ferrocyanide from 50 c.c. of the cyanide solution by means of acidified ferric chloride or sulphate, and titrating with N/100 permanganate.

Oxidisable organic matter in solution is estimated by digesting 50 c.c. of the solution for an hour at 60—70° with a large excess of strongly acidified N/100 permanganate, then cooling, and titrating back with a standard thiocyanate solution, of a strength such that 1 c.c. = 1 c.c. N/100 permanganate. The amount of organic matter is approximately nine times the oxygen consumed in excess of that required by the ferrocyanides and thiocyanates present. The organic matter can be removed by shaking with quicklime and filtering.

Alkalinity.—With N/10 acid and phenolphthaleïn as indicator, all the potassium cyanide, 7·9 per cent. of the potassium zinc cyanide, and the potassium in potassium zinc oxide are estimated; with methyl orange as indicator, all the zinc in potassium zinc cyanide, the zinc and potassium in potassium zinc oxide, and the hydrogen carbonates are estimated. When a caustic alkali or a carbonate is added to a working cyanide solution containing zinc, the following changes ensue: $K_2ZnCy_4 + 4KHO = ZnK_2O_2 + 4KCy$ and $K_2ZnCy_4 + 4Na_2CO_3 + 2H_2O = 2KCy + 2NaCy + ZnNa_2O_2 + 4NaHCO_3$. The hydrogen carbonates have no action on potassium or sodium zinc cyanide, which is only partially decomposed by calcium or magnesium hydroxides, so some alkalinity towards phenolphthaleïn may be due to the former compounds in the presence of potassium zinc cyanide. If lime or magnesia is added to a solution containing sodium hydrogen carbonate and potassium zinc cyanide, the zinc remains in solution as sodium zinc oxide, and the percentage of cyanide is correspondingly increased.

Ferricyanide is estimated by reduction with sodium amalgam and titrating the resulting ferrocyanide.

Sulphide is estimated by agitating with precipitated lead carbonate and titrating with permanganate; loss above that due to ferrocyanides, thiocyanates, &c., is due to the sulphides eliminated.

Ammonia is estimated by precipitating all the cyanide compounds in 10 c.c. with silver nitrate, adding hydrochloric acid, making up to 100, shaking, filtering, distilling 10 c.c. of the filtrate with 150 c.c. of water, and Nesslerising the distillate.

Methods for dealing with urea, oxamide, and formates are under investigation. A few specimen analyses are appended to the paper.

D. A. L.

Estimation of Fusel Oil in Rectified Spirits by Röse's Process. By M. GLASENAPP (*Zeit. angew. Chem.*, 1895, 657—663).—The author has made a thorough investigation of Röse's chloroform process, and finds that, although it works very well for the cruder samples of spirits, it is only by taking extraordinary precautions that trustworthy results can be obtained with the purer kinds. The author's shaking apparatus is made of such a weight and shape that, when filled and plunged into water, it sinks down in a vertical position, so that, after some time, the contents will acquire the exact temperature desired. Even if the measuring tube is most carefully graduated, no two apparatus will agree, unless they are exactly of the same capacity. The reason of this is that, during the shaking, the air becomes saturated with chloroform vapour, and the amount thus lost will be, of course, proportionate to the bulk of the air. Every apparatus must, therefore, be carefully calibrated. Another important item is the time allowed for the chloroform layer to separate; the author advises waiting for at least one hour. The greatest difficulty of all is to obtain a standard alcohol really free from fusel oil, and it is doubtful whether such alcohol has ever, as yet, been obtained. The only plan is to keep on rectifying until the fractions give a constant result when tested in the apparatus. It is also of the utmost importance that the spirit to be tested should be diluted to a sp. gr. of 0·96564 at

15.5°, and for this purpose it is not sufficient to use a Westphal balance, but a very delicate specific gravity bottle should be used. Particular stress is laid on the necessity of thoroughly cleaning the instrument before making a new experiment. A mixture of sulphuric and Nordhausen acid is recommended for this purpose. L. DE K.

Estimation of Sugar. By G. OPPERMAN (*Exper. Stat. Record*, 1895, 7, 184; from *Apoth. Zeit.*, 1895, 10, 216).—The method in which the cuprous oxide is reduced with hydrogen and weighed as copper is modified as follows. The cuprous oxide, filtered in a tube packed with asbestos, is well washed, and dissolved in moderately strong nitric acid, avoiding a great excess. The copper is precipitated electrolytically, washed, dried, and weighed.

N. H. J. M.

Influence of the two Lead Acetates on the Estimation of Invert Sugar by the Fehling-Soxhlet Method. By ARTHUR BORNRÄGER (*Zeit. angew. Chem.*, 1895, 594—596).—The author has tabulated several experiments with invert sugar solutions containing an excess either of lead acetate or of basic acetate.

It appears that, when titrating in the well-known way with Fehling's solution, the presence of decided quantities of lead causes a serious decrease in the percentage of sugar (compare also *Abstr.*, 1895, ii, 143, 296). L. DE K.

Estimation of Cellulose. By GERHARD LANGE (*Zeit. angew. Chem.*, 1895, 561—563).—5—10 grams of the substance, fodder, for instance, is moistened with a little water, mixed with three times its weight of sodium hydroxide and another 20 c.c. of water, and then fused in a large, unglazed, porcelain crucible, partially immersed in an oil bath. After putting on a perforated lid, through which passes a thermometer, the temperature is raised to 175—180°, and kept so for an hour. The principle of the process is that, at this temperature, the cellulose is not chemically acted on by the alkali. After slight cooling, the contents are digested in dilute sulphuric acid, and, after again rendering alkaline with soda, the whole is introduced into a large centrifugal tube and thoroughly whirled. The cellulose rapidly separates, and, after pouring off the supernatant liquid, it is once more washed by whirling with hot water, then washed with alcohol and ether, dried, and weighed. Allowance must be made, as usual, for any mineral matter. If the sample should be rich in fat, this may with advantage be first extracted. L. DE K.

Forensic Chemistry. By GEORG DRAGENDORFF (*Arch. Pharm.*, 1895, 233, 612—630).—The ethereal salts of guaiacol, naphthol, cresol, &c., are readily extracted from their acid aqueous solutions by light petroleum or benzene, but, when mixed with large quantities of organic matter, are best first separated from the latter by means of alcohol.

Guaiacol benzoate (benzosol), when moistened with concentrated sulphuric acid, yields a reddish-purple colour with acetone; with

ferric chloride a violet colour, striped with green and violet-blue; an orange and green colour with nitric acid; a green, violet, and yellow colour with potassium nitrite; a bright red colour with cane or grape sugar; a violet to red colour with Fröhde's reagent; and a violet, green, and blue colour with sulphovanadic acid. Guaiacol salicylate yields a violet colour with ferric chloride and a bright red colour with concentrated sulphuric acid, changing to green, violet, and red on the addition of nitric acid. When moistened with concentrated sulphuric acid, it is coloured green, blue, and red by potassium nitrite, and bright red by acetone. Sulphovanadic acid gives a bluish-black colour, Fröhde's reagent, a violet, changing to green. Guaiacol cinnamate dissolves in concentrated sulphuric acid with a yellow colour, changed to orange by nitric acid, to violet and green by potassium nitrite, and to violet by acetone. Guaiacol cinnamate is less soluble in light petroleum than the salicylate, and is further distinguished from the latter by its ready conversion into benzaldehyde by alkaline permanganate. Guaiacol itself, when pure, dissolves in concentrated sulphuric acid, yielding a colourless solution, which is coloured red to brown by nitric acid, violet and green by potassium nitrite, green by potassium selenate, blue-green and violet by sulphovanadic acid. With Fröhde's reagent, guaiacol yields a green and violet colour; with alcoholic ferric chloride, a blue and emerald-green colour; and with permanganate and hydrochloric acid, a cherry-red to brown colour. It is coloured green by aqueous ferric chloride, and the spectrum of the solution shows an absorption band in the red and orange ($654\text{--}610\mu$), a slight shading at 595μ , and a further slight absorption in the violet and indigo up to 450μ .

Alphol (α -naphthyl salicylate) dissolves in concentrated sulphuric acid with a yellow coloration, changed to blue, green, and red by nitrates and nitrites; conversely, the reaction serves as a delicate test for these salts. The absorption spectrum shows a band from the violet to the green (500μ), and a band in the red ($680\text{--}650\mu$). A mixture of alphol and concentrated sulphuric acid is coloured purple by aqueous furfuraldehyde, and cherry-red by cane sugar, the colour in the latter case being changed to blue by ammonia. The sulphuric acid mixture is turned green by ferric chloride, yellow by acetone, and fluorescent green by iodoform. Fröhde's reagent gives a green coloration with alphol, sulphovanadic acid a green colour, changed to reddish-brown by the addition of water, and sulphuric acid with ammonium uranate green, changing to greyish-brown on heating. Alcoholic alphol is coloured violet by ferric chloride, and, on warming, blue by chloroform and caustic soda.

Betol (β -naphthyl salicylate) dissolved in concentrated sulphuric acid yields a characteristic colour on the addition of a crystal of chloral hydrate, the orange coloration at first produced changing to reddish-violet and then to red with green fluorescence. The other reactions resemble those of its isomeride.

β -Naphthyl benzoate is coloured yellow by concentrated sulphuric acid, but dissolves, on warming, to a violet solution, having a green fluorescence. This solution is coloured dark brown by nitric acid, and, by potassium nitrite, violet, changing to red and blue; it is

coloured violet and red by ferric chloride, bluish-violet by ammonium molybdate, changing to red, green, and blue; violet by Fröhde's reagent and sulphovanadic acid, the colour in the latter case changing to red and blue; green to orange by chloral hydrate, purple to violet by aqueous furfuraldehyde, violet by the sugars, and yellow by acetone. The benzoate is coloured blue when heated with chloroform and alcoholic soda. β -Naphthyllic carbonate gives much the same reactions as α - and β -naphthol.

The tolylic benzoates and salicylates give reactions of the same character as the corresponding salts of guaiacol. The reactions of various amido-derivatives, such as paracetamidophenyllic salicylate, are also described in similar detail. JN. W.

Detection of Formaldehyde. By G. ROMYN (*Ned. Tydschr. Pharm.*, &c., 1895, 7, 169—175).—The article of food, milk for instance, is submitted to distillation. Although a portion of the formaldehyde is retained by the albuminous matters, a little of it is sure to pass over with the distillate, and may then be identified as follows. A drop of the liquid is mixed on an object glass with a drop of ammonia, and evaporated to dryness; the crystalline residue, when examined under the microscope, will be found to consist, not of rhombohedra, but of regular crystals if formaldehyde was present. It is then moistened with water, and treated with either of the following reagents.

Mercuric chloride in excess at once gives a precipitate; in a short time, three, four, or six-sided stars are noticed, afterwards octahedra. This test still shows at a dilution of 1—100,000.

Potassium mercuric iodide and dilute hydrochloric acid give hexagonal, six-angled, pale-yellow stars; this reaction is obtained at a dilution of 1—10,000, but not when it reaches 1—100,000.

Platinic chloride gives regular octahedral crystals, much resembling ammonium platinochloride, but darker in colour; the reaction is just visible at a dilution of 1—10,000.

Phosphomolybdic acid gives right, rhombic crystals, very characteristic at a dilution of 1—10,000.

Potassium bismuth iodide and dilute hydrochloric acid gives regular crystals, mostly octahedra. The yellow precipitate is formed at once, at a dilution of 1—1,000; but only slowly when at a dilution of 1—10,000.

Stannous chloride and strong hydrochloric acid give rhombic needles and crystals. The reaction is very strong in a 1 per cent. solution, and just visible when at a dilution of 1—1,000.

Potassium iodide containing iodine gives rectangular plates and aggregations of the rhombic system, very distinct at a dilution of 1—1,000, but no longer visible at 1—10,000.

Picric acid gives needles, probably rhombic. When the dilution reaches 1—1,000, they only form after some time. L. DE K.

Volatility of Fatty Acids and Laws Deduced therefrom. By HENRY DROOP RICHMOND (*Analyst*, 20, 193—198; 217—219).—The author has tabulated a number of results obtained by distilling the

mixed fatty acids of butter under varying conditions, and mathematical equations are given to explain the results. It appears that in the well-known Reichert-Wollny process only about 87 per cent. of the total volatile acids is found in the distillate. L. DE K.

Estimation of Uric acid in Urine. By MARTIN KRÜGER (*Zeit. physiol. Chem.*, 1895, 21, 311—318).—The following method, based on the author's previous work, is recommended. One hundred c.c. of urine is taken, and the nitrogen of the uric acid, *plus* that of alloxuric bases, estimated. This is done by adding to the boiling urine 10 c.c. of sodium hydrogen sulphite solution, 10 c.c. of copper sulphate (10 per cent.) solution, and 5 c.c. of barium chloride (10 per cent.) solution. The mixture is boiled for three minutes, and allowed to remain two hours; the precipitate is then collected, washed with hot water, and its nitrogen estimated by Kjeldahl's method. In another specimen, the urine is first freed from uric acid by adding sodium carbonate until a flocculent precipitate forms, and then 5 c.c. of 10 per cent. acetic acid is added. The nitrogen of the alloxuric bases is then estimated, and this, subtracted from the nitrogen obtained in the first experiment, gives the uric acid nitrogen by difference.

There are various safeguards introduced when this is applied to pathological urines. The results given come out very nearly the same as those obtained by the standard Salkowski-Ludwig process.

W. D. H.

Iodine and Bromine Absorptions of Linseed Oil. By ROWLAND WILLIAMS (*Analyst*, 20, 276—277).—The author states that the iodine absorption of raw linseed oil is much higher than is generally believed. An examination of several hundred samples of undoubtedly genuine origin gave figures varying from 180 to 190 per cent. of iodine. The author attributes the low figures of other observers to the fact, which is not sufficiently appreciated, that it is absolutely necessary to use a large excess of the Hübl reagent, and to let this act for at least 18 hours.

As regards the bromine absorption, the author strongly recommends the gravimetric process proposed by Hehner (*Abstr.*, 1895, ii, 428), as the results are more trustworthy than those obtained by the volumetric method. When applying the iodine or bromine absorption process to the assay of boiled linseed oil, it must be remembered that both absorptions are considerably lessened by the boiling.

L. DE K.

Saponification in the Cold. Saponification Numbers and Reichert-Meissl Numbers. By ROBERT HENRIQUES (*Zeit. angew. Chem.*, 1895, 721—724).—The author recommends the following modification of the Reichert-Meissl process. Five grams of the fat is put into a porcelain dish, and dissolved in 25 c.c. of light petroleum, 25 c.c. of 4 per cent. alcoholic soda is added, and the dish is covered, and allowed to remain over night; the liquid is then evaporated to complete dryness on the water-bath, and the powder transferred to the distilling flask. After rinsing the basin with the prescribed amount of water, the process is conducted as usual. No volatile ethereal salts are formed in the cold process. The small amount of carbonic

anhydride absorbed from the air does not influence the result. The process may also be used for taking the saponification number; for this purpose the fat is dissolved in a stoppered flask as directed, allowed to remain for 24 hours, and the excess of alkali titrated; if the mass should have become somewhat too solid, the addition of some more alcohol and gentle warming will be found useful. Wax must be dissolved in hot, light petroleum (boiling point, 100—150°) before adding the soda.

L. DE K.

Estimation of Tannin in Wines. By E. MANCEAU (*Compt. rend.*, 1895, **121**, 646—647).—No method of precipitation with soluble gelatin or a metallic salt will remove the whole of the tannin from a solution; this can only be effected by means of animal membranes, such as the gut cords used in Girard's process. The sensitiveness required in dealing with dilute solutions like wines is obtained by combining Girard's process with the use of permanganate.

One hundred c.c. of champagne or other wine containing a similar quantity of tannin (or of stronger wines previously diluted with a known volume of water) is allowed to remain in contact with 1 gram of gut cords for about a week in a well-closed flask. The liquid is then titrated by means of permanganate solution, 1 c.c. of which is equivalent to 0.02 milligram of pure gallotannin, indigo solution being used as the indicator. The difference between the volumes of permanganate solution required by a given volume of wine before and after the removal of the tannin gives the quantity of œno-tannins present, in terms of gallotannin. In champagnes, the quantity varies from 8 milligrams to 50 milligrams per litre.

The gut cords for this process are prepared by washing uncoiled violin strings with dilute alcohol, dilute acids, and water until these solvents no longer remove anything that reduces potassium permanganate.

C. H. B.

Titration of Alkaloids with Iodine Solution. By CARL KIPPENBERGER (*Zeit. anal. Chem.*, 1896, **35**, 10—27).—In a former paper (Abstr., 1895, ii, 465), it was stated that when a salt of an alkaloid is mixed with a solution of iodine in potassium iodide, only the free iodine is concerned in the formation of the alkaloid periodide, Alk,HI,I_2 , three atoms of iodine being consumed for each molecule of alkaloid. The author now investigates the reaction more closely. When the iodine solution is prepared with the smallest possible quantity of potassium iodide, the results present considerable irregularities: the precipitate contains free iodine in larger or smaller amount as the excess of iodine solution used is larger or smaller; the amount of potassium iodide decomposed is sometimes larger and sometimes smaller than would correspond with the equation $\text{Alk,HCl} + \text{KI} + \text{I}_2 = \text{Alk,HI,I}_2 + \text{KCl}$: and the amount of free iodine consumed is considerably larger than is the case when more iodide is present. By adding either a large excess of hydriodic acid or of potassium iodide, especially when the free acid in the alkaloid solution has been nearly neutralised, the consumption of free iodine falls, in the case of strychnine, to 2 atoms. With narcotine

and atropine, the amount consumed is always more than 2 atoms, and varies somewhat with the conditions. For alkaloids other than strychnine, it is therefore best to standardise the iodine solution against known quantities of alkaloid under circumstances as closely as possible resembling those of the titration itself; but on this subject a further communication is promised.

M. J. S.

Estimation of Creatinine in Urine. By RUDOLF KOLISCH (*Chem. Centr.*, 1895, i, 814—815; from *Centr. inn. Med.*, **16**, 265—269).—The estimation of creatinine has as yet received but little appreciation on account of the very imperfect analytical methods. The author proposes a new process. Two hundred c.c. of urine is precipitated with 20 c.c. of a mixture of calcium chloride and milk of lime and filtered. Two hundred c.c. of the filtrate is acidified with acetic acid, evaporated to a thick syrup, and the residue while still warm is exhausted four or five times with alcohol. The solution is diluted in a graduated flask to 110 c.c., and 100 c.c. is then used for precipitation with mercuric chloride solution, after first acidifying with acetic acid. This mercury solution is prepared by dissolving 30 grams of mercuric chloride, 1 gram of sodium acetate, and 3 drops of acetic acid in 125 c.c. of absolute alcohol.

After adding enough of this solution to precipitate all the creatinine, the precipitate is washed on a filter with absolute alcohol containing a little sodium acetate until the washings no longer become turbid when neutralised, showing that all the urea has been removed. The creatinine is now calculated from the amount of nitrogen contained in the precipitate, which is best estimated by using Kjeldahl's process. Its percentage is finally found by multiplying by 100/81.

L. DE K.

Assay of Opium. By DAVID B. DOTT (*Pharm. J. Trans.*, 1894, [3], **24**, 847).—Ten grams of powdered opium is digested with 25 c.c. of water, 1.8 grams of barium chloride dissolved in 12 c.c. of water added, and the whole made up to 50 c.c., mixed, and, after a short time, filtered. To half the filtrate, representing 5 grams of opium, just enough sulphuric acid to precipitate the barium is added, and to the filtrate from this, enough ammonia to neutralise the free acid. The solution is then concentrated to 6—7 c.c., and allowed to cool; 1 c.c. of alcohol and 1 c.c. of ether are next added, then ammonia in slight excess. After three hours, the precipitate is collected on a tared filter, dried, washed with benzene or chloroform, dried, and weighed. It is then titrated with N/10 acid, until the morphine is neutralised, as indicated by the solution reddening litmus paper. One c.c. of N/10 acid = 0.0303 gram of morphine hydrate.

R. R.

Estimation of Aconitine. By JOHN C. UMNEY (*Pharm. J. Trans.*, 1895, [3], **25**, 860).—A definite weight of aconitine is hydrolysed by heating on a water bath for two hours with a known volume of a standard alcoholic solution of caustic alkali in a reflux apparatus. By this treatment, it is resolved into aconine, and acetic and benzoic acids, the latter combining with the alkali present; the amount of the acids

can then be found by titrating the uncombined alkali. The solution is again made alkaline, the alcohol evaporated off on a water bath, and sufficient hydrochloric acid added to separate the benzoic acid, which is extracted by successive washings with ether, weighed, and the quantity of alkali required for its neutralisation in the first part of the process calculated. By deducting this from the total amount, the quantity of acetic acid is found, and the amount of crystalline aconitine is thus determined.

R. R.

Assay of Ipecacuanha. By RICHARD A. CRIPPS (*Pharm. J. Trans.*, 1895, [3], 25, 1093—1094).—The author refers to Paul and Cownley's investigations, and mentions the presence in ipecacuanha of a fourth alkaloid, noted by himself in 1891; he has sought in vain for Arndt's volatile alkaloid. He finds that the proportion of the third alkaloid to the emetine and cephaeline taken together may vary from one-twentieth to one-fourth, and thinks that ipecacuanha, like other drugs containing several alkaloids, contains them in varying proportions. In an assay, therefore, the total alkaloids should be taken into account. Lyons' process should be the one recognised, and only the Brazilian root be official, this being required to yield not less than 2.0 nor more than 2.5 per cent. of alkaloids. A table shows many different assays and their divergent results.

R. R.

Ehrlich's Diazo-reaction. By RICHARD T. HEWLETT (*Brit. Med. J.*, 1896, i, 136—137).—Several modifications have been proposed in the original method of testing with sulphanilic acid and sodium nitrite. The reaction is invariably given by the urine in typhoid fever, although occasionally it is seen in other diseases also.

Attention is drawn to the fact that the test solutions must be freshly prepared before using.

The nature of the substance in the urine that gives the reaction is uncertain, and of a large number of materials examined, morphine was the only one which gives a similar red reaction, but no green precipitate forms on standing. One part of morphine in 10,000 of water gives the test.

W. D. H.

Colour Reactions of Proteïds with Nitrous acid and Phenols. By KARL LANDSTEINER (*Chem. Centr.*, 1895, i, 695; from *Centr. f. Physiol.*, 8, 773—774).—The colour obtained by the action of nitrous acid and phenols on proteïds is attributed by Obermayer to the formation of diazo-compounds. The author, however, explains the reaction as follows: By acting on the hydrochloric acid solution of tyrosine, first with nitrous acid, then with alkali, and finally with α - or β -naphthol, a bluish-red colour is obtained. This reaction is not caused by the amido-group contained in the tyrosine, as para-hydroxybenzoic acid also gives the test. Proteïds undoubtedly first yield tyrosine when the reaction is applied.

L. DE K.

General and Physical Chemistry.

Relation between the Intensity of Light and its Action on Mixtures of Ferric Chloride and Oxalic acid. By GEORGES LEMOINE (*Compt. rend.*, 1895, **121**, 817—819).—The author has investigated the relation between the visual intensity of light and its action on mixed solutions of ferric chloride and oxalic acid, using a system of two large polarising prisms as a means of varying the intensity of the light incident on the small cell containing the liquid. He finds that the chemical change produced is proportional to the visual intensity of the light; that there is no sensible "period of induction," the result being the same whether an exposure of a given total duration is intermittent or continuous; and that on cloudless days, the visual intensity of the sunlight remains practically constant for comparatively long periods (compare Abstr., 1895, ii, 249).

C. H. B.

New Molecular Refraction Formula. By F. ZECCHINI (*Gazzetta*, 1895, **25**, ii, 269—284).—The author has calculated the observed and theoretical molecular refractions of a long series of compounds of different types, using the formula $\frac{n^2 - 1}{(n^2 + 2)d}$. The values calculated from the set of atomic refractions given, agree well with the observed molecular refractions, but the formula is not independent of the temperature.

W. J. P.

Relations between the Composition and Absorption-spectra of Organic Compounds. By GERHARD KRÜSS (*Zeit. physikal. Chem.*, 1895, **18**, 559—562).—An addition to the late author's previous communication on this subject (Abstr., 1888, 1141). The paper contains the observations on the absorption-spectrum in the case of alizarin, purpurin, quinizarin, hystazarin, anthraflavic acid, and a number of their derivatives.

L. M. J.

Anomalies in the Rotatory Dispersion of Malic acid. By RAFFAELE NASINI and G. GENNARI (*Zeit. physikal. Chem.*, 1896, **19**, 113—129).—Anomalies having been previously observed in the rotation of this acid, the authors investigated the optical phenomena by means of a Landolt-Lippich polarimeter. The effects of temperature, concentration, and of the addition of boric acid, in aqueous solutions were investigated, and solutions were examined in methylic, ethylic, and propylic alcohols, and in acetone. The phenomena in aqueous solutions were very complicated; dilute solutions were lævorotatory and normal; by increase of concentration, a lævorotatory, achromatic solution was first obtained, then a lævo-maximum in the yellow, after which the more refrangible rays gave a dextrorotation, whilst for the highest concentrations, the solutions were normally dextrorotatory. Increase of temperature had an effect analogous to dilution, whilst in the organic solvents the dilute solutions were lævorotatory, but the

concentrated solution gave dextrorotations for the more refrangible rays. It is evident that such variations are associated with great changes in the dispersion. The probable cause of these results is discussed; the presence of two compounds of different dispersion coefficients and opposite rotatory power is sufficient to explain the results, but the nature of the two compounds does not seem clear. The authors do not consider as probable the formation of hydrates, or polymerides, or the existence of "crystalline molecules" (compare Abstr., 1893, ii, 103), neither does dissociation appear entirely satisfactory. The explanation regarded as most probable is that of a specific action of the solvent in which the molecular dissymmetry is altered or destroyed, so that the compound may acquire physical properties approximating to those of its ions without being actually dissociated. In the alcoholic solutions, in an analogous manner, the approximation is to the lævorotatory ethereal salts of malic acid (Abstr., 1895, ii, 251). L. M. J.

Rotatory Dispersion of Nicotine and its Salts. By G. GENNARI (*Gazzetta*, 1895, 25, ii, 252—257; also *Zeit. physikal. Chem.*, 1896, 19, 130—134).—In continuation of the work of Gennari and Nasini (this vol., ii, 133), the author has examined the specific rotations of nicotine, and its sulphate, hydrochloride, and acetate under various conditions of concentration and solvent, for five different wave-lengths, using Landolt's ray filters.

At 20°, pure nicotine of sp. gr. = 1.01071 at 20°/4° has the specific rotations of -123.37° , -162.84° , -209.78° , -250.71° , and -317.79° , for the ray filter colours *rt*, *D*, *gr*, *hb*, and *db* (compare Abstr., 1895, ii, 1) respectively; the specific rotations are considerably lower in benzene and ethylic and methylic alcoholic solutions, and very much lower in aqueous solutions, the specific rotation diminishing as the dilution increases. The solutions, however, are all lævorotatory, and the coefficients of rotatory dispersion calculated as $[\alpha]_x/[\alpha]_y$ for the various rays are the same for nicotine, both pure and in solution. The specific rotations of the various salts examined at 20° are given in the following table.

Salt.	Concentration, per cent.	$[\alpha]_{rt.}$	$[\alpha]_D.$	$[\alpha]_{gr.}$	$[\alpha]_{hb.}$	$[\alpha]_{db.}$
Sulphate.....	31.420	+12.19	+15.66	+19.20	+21.82	+24.74
Hydrochloride...	18.414	+12.13	+15.45	+18.72	+21.88	+23.84
Acetate.....	24.276	+13.00	+16.96	+20.40	+23.50	+25.84

It will be seen that the salts are all dextrorotatory in aqueous solution, and the rotatory dispersions are found to be less than those of nicotine itself.

A mixture of nicotine and acetic acid, in molecular proportion, is strongly lævorotatory, but, on gradual dilution with water, the lævorotation decreases until the solution becomes highly dextrorotatory. This can only be explained by supposing that, as the acetic acid solu-

tion is diluted, more and more of the dextrorotatory acetate is formed, whilst the proportion of lævorotatory base decreases. W. J. P.

Rotatory Power of Superfused Rhamnose. By DÉsirÉ GERNEZ (*Compt. rend.*, 1895, **121**, 1150—1152).—The specific rotatory power of rhamnose at 18° is -6.5° a minute after dissolution, but attains the constant value of $+9.75^\circ$ in less than an hour. Direct measurements of the sp. gr. and specific rotatory power of the superfused rhamnose, ($C_6H_{12}O_5 + H_2O$) gave the following results.

t° .	0°.	16°.	18°.	19°.	46°.	70°.	73°.	100°.
Sp. gr.	1.400	1.388	1.387	1.386	1.357	1.349	1.346	1.325
Sp. rot. power..	9.28°	8.66°	8.59°	8.53°	7.57°	6.73°	6.64°	5.70°

The observations are accurately represented by the expression

$$[\alpha]_D^t = 9.22^\circ - 0.03642t + 0.0000123t^2.$$

The rotatory power of the superfused rhamnose diminishes regularly as the temperature rises, and at 100° has only 61 per cent. of its value at 0°. Its specific rotatory power in aqueous solution is not identical with that of the superfused substance, and this difference must be taken into account in any attempts to explain multirotation.

C. H. B.

Flames and Illuminating Gases. By JOSEF M. EDER (*Zeit. physikal. Chem.*, 1896, **19**, 20—24).—The author criticises various points in Bohn's communication (this vol., ii, 140), and calls attention to the fact that several of the observations and conclusions had been previously recorded by himself.

L. M. J.

Luminosity of pure Inorganic Compounds and of Solid Solutions. By EILHARD WIEDEMANN and GERHARD C. SCHMIDT (*Zeit. physikal. Chem.*, 1895, **18**, 529—552).—Many inorganic, as well as organic, compounds (this vol., ii, 86) become luminous when subjected to the influence of the cathode rays, frequently exhibiting also an after-luminosity, and possessing the property of again becoming luminous when heated. The effect of the cathode rays on pure compounds is first considered, and tables of the luminosity phenomena are given. The luminosity colour of the salts appears to be dependent on the metal, the acid only influencing the intensity of the light. In solid solutions, a small quantity of the dissolved substance may cause a great alteration of the colour and intensity, both of which are also dependent on the solvent, whilst the intensity is, in dilute solution, a direct function of the concentration. The previous heating of the compound almost invariably influences the phenomena, either owing to chemical changes so occasioned, or to alteration of the physical state, whilst the after-luminosity is also of longer duration. At high temperatures, the luminosity still remains, but the after-effects decrease or disappear, and the colour usually changes to a more refrangible shade, whilst at low temperatures, the luminosity is brighter and the after-effect of longer duration. The physical modification which is produced by these cathode rays appears to be usually of a fairly stable nature, being only destroyed by relatively high

temperatures (200° and above), whilst at ordinary temperatures the thermo-luminosity may last over six months, although in some cases it is lost in a week. The addition of foreign substances may cause either an increase or a decrease of luminosity, both in the case of pure compounds and of solid solutions. Experiments on phosphorescence showed that the phosphorescence colour is the same as that of the cathodic luminosity, and that it also is frequently destroyed by foreign substances, whilst Stokes' rule was found to be valid for all the solid solutions examined. The paper concludes with a brief theoretical consideration of the observed facts.

L. M. J.

Dependence of the Dielectric Constant on Temperature and Pressure. By FLORIAN RATZ (*Zeit. physikal. Chem.*, 1896, 19, 94—112).—The dielectric constant was determined at various temperatures and pressures by Nernst's method (*Abstr.*, 1894, ii, 437), in the case of benzene, toluene, carbon bisulphide, ethylic ether, chloroform, aniline, amyl alcohol, ethylic alcohol, and water. The value $(D - 1)/(D + 2)d$ is a function of both temperature and pressure, the temperature coefficient increasing with the dielectric constant. The variation between the values of the constant obtained from the formula and the actual number is, for a temperature of 30°, below 10 per cent., and the value of the above expression within 40° changes by less than 5 per cent. The temperature coefficient is small, and in all cases negative, decreasing slightly as the temperature rises. No maximum for D is found at 4° in the case of water, and if such exists at all, it must be between 0° and 1°. In all cases, the value of D is greater than A^2 obtained from refraction observations. The pressure coefficient is small and positive, so that it follows that the influence of temperature is greater, and that of pressure less, than the calculated effect. Details of the method, the purification of the compounds examined, and the experimental numbers are given in the paper.

L. M. J.

The Dilution Law of Electrolytes. By LUDWIG STORCH (*Zeit. physikal. Chem.*, 1896, 19, 13—19).—The author has obtained a dilution law of the form $\left(\frac{\mu}{v\mu_\infty}\right)^x = k\left(\frac{\mu_\infty - \mu}{v\mu_\infty}\right)^m$,* where μ_∞ and μ are the molecular conductivities at infinite dilution and volume v respectively. This may be expressed as $x \log(\mu/v) = \log(\mu_\infty - \mu/v) + \log(k\mu_\infty^{x-1})$. By the construction of curves with Kohlrausch's values for μ/v , and a probable μ_∞ , values for x and $(k\mu_\infty^{x-1})$ are obtained, and hence, by recalculation, the actual value of μ_∞ . The value for x differs for different electrolytes, but in the 12 cases considered varies only between 1.400 and 1.577, and the conductivities then calculated from the formula agree very closely with the observed numbers. It is seen that the above formula for the value $x = 1.5$ is identical with that obtained by van't Hoff from Rudolphi's numbers (compare this vol., ii, 145). For very high concentrations, however, the formulæ

* There appear to be misprints in the formulæ as printed in the *Zeitschrift*; the equation given is obtained by recalculation from the final form.

are not valid; thus, from $v = 0.33, 1$ and 2 , the values $x = 1.699$ $\mu_{\infty} = 104$ were obtained for potassium chloride, the corresponding values derived from $v = 10$ to 16667 being 1.435 and 122 ; the lower values for μ_{∞} probably indicate the presence of double molecules in the more concentrated solutions.

L. M. J.

Specific Heats of Solutions. By GUSTAV TAMMANN (*Zeit. physikal. Chem.*, 1895, **18**, 625—644).—Observations have shown that the heat capacity of solutions, if not too dilute, is generally smaller than that of the two components, and frequently less than that of the water alone. The heat capacity of the water has, however, been calculated without due provision for the alteration of the specific heat, owing to the change in the internal pressure. The alteration of specific heat by pressure change being given by the equation $(dC/dp)(T \text{ const.}) = -T(d^2v/dT^2)(p \text{ const.})$, that due to the solution in water of any compound is given by a similar equation, where $p = \Delta K$; the alteration of internal pressure (see Abstr., 1895, ii, 307, and previous abstracts). If the expansion of the solution be given by $v = A + at + bt^2$, which holds for small temperature changes, then $d^2v/dt^2 = 2b$, and is determined from Amagat's experiments to be a linear function of p , and the value is obtained at various temperatures. The value for the specific heat is thus obtained, and, on adding the heat capacity of the water to that of the salt in solutions of potassium chloride, bromide, iodide, nitrate, and hydroxide; hydrogen chloride, nitric and sulphuric acids; sodium sulphate, nitrate, and hydroxide; ammonia, ammonium sulphate, magnesium sulphate, and barium chloride, results are obtained in very close approximation to the experimental determinations, except in the cases of sodium chloride and sulphuric acid. The changes due to alteration of ΔK with temperature are considered, but cause no appreciable difference. Similar reasoning is applied to the cases of neutralisation, where the heat capacity of the salt solution formed is not the sum of those of the added acid and base together with that of the water formed by neutralisation. When corrections due to the alteration of internal pressure are applied, concordant results are obtained. The changes in the specific heat of solutions due to temperature alterations are also considered, and found to be of the order indicated by the early experiments of Marignac.

L. M. J.

Relationship of the Heats of Vaporisation of Gases to their Densities, and also to their Boiling Points. By WILLIAM L. DUDLEY (*J. Amer. Chem. Soc.*, 1895, **17**, 969—986).—The author has proved, by a series of experiments on substances belonging to the fatty and aromatic series, that in any homologous series the heat of vaporisation in a unit of volume of the vapour under the same conditions as to temperature and pressure is proportional to the density, and also to the absolute boiling point.

The characteristic of the curve is dependent on the acid radicle; that is, the acid radicle is the basis of the structure of the molecule, and the bases in combination with it do not alter the general molecular architecture.

L. DE K.

The Physical Alteration of certain Sulphur Compounds at Temperatures below their Melting Points. By WALTHÈRE SPRING (*Zeit. physikal. Chem.*, 1895, **18**, 553—558).—Experiments analogous to those undertaken with metals (Abstr., 1895, ii, 37) were made on the sulphides of silver, arsenic, antimony, bismuth, copper, tin, cadmium, lead, and zinc. The amorphous sulphides obtained by precipitation were used, being first washed, dried, and *lightly* pressed into cylinders. The latter treatment was merely to bring the particles into contact, the pressure being so slight that the cylinders could be easily crumbled between the fingers. One half of the cylinder was kept for comparison, the other enclosed in an exhausted glass tube and exposed for nine days of 7—8 hours to a temperature of 265° (150° for the arsenic sulphide). The cylinder of silver sulphide, after this treatment, was steel grey, with a metallic lustre, and with crystal faces visible on the surface. It could not be broken by the hand, and, after forcible breaking, exhibited a crystalline fracture resembling that of steel. Similar results were also obtained with the other compounds. Uncompressed powders were also employed, which formed compact masses, with, usually, indications of a crystalline nature. The author points out the probable importance of these results in geology, as they indicate the possible formation of crystalline rocks, &c., without fusion or the aid of a solvent. L. M. J.

Melting Point of Organic Compounds. By BERNHARD VON SCHNEIDER (*Zeit. physikal. Chem.*, 1896, **19**, 155—158).—The melting points of a number of organic compounds were determined by the use of an alcohol thermometer and a freezing mixture of solid carbonic anhydride and ether. Corrections for the hotter portion of the stem are applied, and the following results obtained.

Ethylie oxalate	—41·0°	Benzonitrile	—12·9°
Ethylene dichloride.	—36·0	Diethylaniline	—38·8
Ethylene chlorobromide	—16·6	Paraphenetidine	+ 2·4
Ethylene chloriodide	—15·6	Orthonitrotoluene	—14·8
Chlorobenzene	—45·0	Anisole	—37·8
Bromobenzene	—30·5	Ethylthiocarbimide	—5·9
Iodobenzene	—28·5	Chloropierin	—69·2
		Ethylie salicylate	+ 1·3

L. M. J.

The Apparent and True Freezing Point, and Freezing Point Methods. By MEJER WILDERMANN (*Zeit. physikal. Chem.*, 1896, **19**, 63—93).—The expressions deduced by Nernst and Abegg (Abstr., 1895, ii, 155) are incomplete, inasmuch as they do not take into account the heat (i) evolved by the precipitation of ice, (ii) absorbed by its solution. In the case of an air bath, the course of the temperature change owing to radiation, &c., is $dt/dz = c(t_z - t)$; that owing to stirring is $dt/dz = k'$, hence $dt/dz = c(t_z - t) + k'$ (i); and at the convergence temperature t_s , $dt/dz = c(t_z - t_s) + k' = 0$, and $t_s = t_z - k_1/c$, where t_z is temperature of the air bath and z the time, so that (i) becomes $dt/dz = c(t_s - t)$, agreeing with Nernst's deduction. If t_s is above the freezing point, then melting of ice occurs,

and if t_f and t_o are the temperatures of the liquid and freezing point respectively, $dt/dz = k(t_o - t_f) + c(t_s - t_f)$; hence, when the temperature is constant, $t' = t_o + \frac{c}{k}(t_s - t')$, and t' the observed temperature must be higher than t_o , the actual freezing point, and less than t_s , the convergence temperature. In order that $(t_s - t')c/k$ may be small, c must be as small as possible, that is, the volume of the liquid should be great, and k should be large, which means that the surface of the ice should be great, and the ice, therefore, in fine needles and as large as possible, so that those determinations in which the readings are taken when the ice specks disappear are the worst possible. As the same formula applies to both pure water and the solution, the observed depression is given by $t_o - t'_o = \left(1 + \frac{c}{k}\right)(t' - t'')$ (if the values of c and k are equal for solution and pure water); so that the apparent values bear to the true values a constant ratio at all concentrations, if not too great. In the author's experiments, the results are hence only 0.1 per cent. too small, and the greatest error due to this cause in the work of various observers appears to be about 0.0048°. The author points out also the bearing on the results of the presence of an ice cap (compare Trans., 1895, 6, and Abstr., 1895, ii, 105).

Where the convergence temperature is below the freezing point, the temperature change is given by $dt/dz = c''(t_o - t_f) + c(t_s - t_f)$, which, by equating to zero, yields $t' = t_o + \frac{c}{c''}(t_s - t')$, so that t' lies between t_o and t_s . Experiments to find the value of the constants here and in the previous formulæ are recorded, and the result obtained that for a bath at -5° the value $c/c''(t_s - t')$ would not reach 0.003°, whilst for the freezing point depressions, that is, the difference of the corrections for solvent and solution, the values become still less. In this case, also, it is pointed out that the necessity of avoiding an ice cap no longer exists. L. M. J.

Method for the Determination of the Freezing Points of Concentrated Solutions. By MAX ROLOFF (*Zeit. physikal. Chem.*, 1895, 18, 572—584).—The freezing point is determined by finding the composition of the solution which, at a determined constant temperature, remains in equilibrium with ice. The chief difficulty is the maintenance of the freezing mixtures at a sufficiently constant temperature, but this is overcome by the use of "cryohydrates" jacketed by colder freezing mixtures. Experiments with hydrogen chloride included observations on 22 solutions varying in concentration from 1.42 per cent. to 16.98 per cent. The molecular depression was found to increase from 36.7 to 61.9, a result accounted for by the positive heat of dilution of the solution. The values are compared with those obtained by Nernst, Jones, and Le Blanc and Noyes, the agreement being very close. In the case of potassium chloride solutions, the molecular depression decreased from 34.3 at 0.836 per cent. to 32.6 at 24.62 per cent., the values being again in satisfactory

accord with those of Jones and Kistiakowsky. From the values also the osmotic pressures are calculated by means of the expression deduced by Arrhenius, the numbers being in satisfactory accord with those obtained by Dieterici from the alteration of the vapour pressures. By use of the values found for the osmotic pressure, the ratios of the vapour pressures of solvent and solution are also calculated, the numbers being in agreement with the measurements of Dieterici, Fischer, and Tammann, but not with those of Juhlin and Ramsay and Young. Researches with acetic acid gave a value for the molecular depression which decreased from 19.4 to 10.0, the fall below the normal value 18 being probably due to the formation of complex molecules.

L. M. J.

The Freezing Points of Dilute Solutions. By WALTHER NERNST and RICHARD ABEGG (*Zeit. physikal. Chem.*, 1895, **18**, 658—661).—A reply to Jones (this vol., ii, 155), in which the authors point out that the correction of 20 per cent. must be allowed if found to be theoretically valid. Further the variations of 5 per cent. in their values for the sodium chloride depression are still within the errors of observation, and that the increase in the molecular depression of ethylic alcohol is also within the limits of observation.

L. M. J.

Exceptions to the Law of Freezing Point Depressions. By FELICE GARELLI (*Gazzetta*, 1895, **25**, ii, 173—178).—In continuation of the previous work of Garelli and Montanari (*Abstr.*, 1895, ii, 205) on the anomalous depressions of the freezing point of a solvent produced by a dissolved substance of similar constitution, the author has examined the behaviour of a number of organic substances in various solvents.

Using paraxylene as the solvent (compare Paternò and Montemartini, *Abstr.*, 1895, ii, 207), normal depressions are obtained with naphthalene, pyrroline, and piperidine; $\alpha\alpha$ -dimethylpyrroline and $\alpha\alpha$ -dimethylthiophen, however, in paraxylene, give molecular weights which are too high, just as pyrroline and thiophen do in benzene solution. Similarly, $\alpha\alpha$ -dithionyl gives too high a molecular weight in diphenyl solution, whilst it behaves quite normally in freezing benzene (compare Auwers, *Abstr.*, 1895, ii, 41).

Substances which are geometrical or position isomerides do not seem to form isomorphous mixtures or solid solutions, and therefore the one depresses the freezing point of the other quite normally. Thus apiol dissolved in isoapiol, and isocrotonic acid dissolved in crotonic acid give the theoretical molecular weights; the same is true of pyrocatechol and quinol dissolved in resorcinol. The molecular depression of the freezing point of resorcinol is found to be 65.

W. J. P.

Cryoscopic Behaviour of Substances of similar Constitution to the Solvent. By FELICE GARELLI (*Gazzetta*, 1895, **25**, ii, 179—188).—Anomalous cryoscopic behaviour may in any particular case be due to one of two causes. Some substances, such as alcohols, oximes, or phenols, which contain hydroxyl, tend to form complex

molecular aggregates when dissolved in hydrocarbons, and their molecular weights approximate to the theoretical ones only in dilute solutions; further, when the dissolved substance and the solvent have analogous constitutions, a solid solution is formed as the solvent freezes out, and the results give no indication of the true molecular weight of the dissolved substance. Since both these causes may bring about anomalies, Paternò's criticisms (this vol., ii, 156) of Garelli and Montanari's previous results (Abstr., 1895, ii, 205) lose considerably in force; the fact that phenol and paraxyleneol behave abnormally both in benzene and paraxylene solutions is not surprising, as phenol would tend to form solid solutions in benzene solution, whilst in paraxylene solution it would tend to form molecular aggregates. The kind of abnormalities observed are in agreement with this view.

The observation of Ampola and Manuelli (this vol., ii, 238) that chloroform has the normal molecular weight in bromoform solution is not at variance with the author's views, for he has not hitherto observed the formation of solid solutions amongst aliphatic compounds (Abstr., 1894, i, 157); it may also be remarked that chlorobenzene and bromobenzene behave quite normally in benzene solution.

W. J. P.

The Cryoscopic Behaviour of Substituted Phenols in Naphthalene. By KARL AUWERS [and W. R. INNES] (*Zeit. physikal. Chem.*, 1895, 18, 595—624).—Cryoscopic experiments on hydroxy-compounds in benzene have been previously recorded (Abstr., 1894, ii, 133; 1895, ii, 41), and the observations are here extended to solutions of such compounds in naphthalene. In order to prevent changes in the thermometric readings due to alteration of the freezing point, the thermometers were maintained between the experiments at a temperature of 80°, that is, close to that of the actual experiments. The molecular depression for naphthalene being uncertain (previous determinations varying from 85 to 70), it was redetermined by experiments with benzile, benzilosazone, and ethylic ethanetetra-carboxylate. The values thus obtained vary between 68·25 and 69·3, mean 68·92, agreeing well with the value 69, calculated by van't Hoff's formula, which is afterwards employed.

Experiments were made with 52 homologous and substituted phenols, and the following general relations observed. (I) Ortho-substituted phenols are cryoscopically normal, para-derivatives abnormal, whilst meta-derivatives occupy an intermediate position, but approximating more towards the para-compounds. (II) A substituting group in the ortho-position may hence be said to exert a "normalising" influence, the reverse obtaining for a group in the para-position, the extent of this influence depending on the nature of the group. In this respect, the aldehyde group CHO exerts the greatest influence; then in order—carboxalkyl, COOR; nitro-group; halogens; alkyls. (III) Other conditions being similar, the ortho-group has a stronger influence than the para- or meta-, so that, for instance, ortho-nitrophenol is normal, para-nitrophenol abnormal, and orthopara-dinitrophenol normal. The cryoscopic behaviour of a com-

pound, therefore, unless further observations prove the rules to be not general, may be used to determine the constitution or orientation. The cause of these peculiarities is very uncertain, but the author points out some possible explanations. The abnormal values may be due to double molecules; these are not formed, however, in the case of ortho-compounds owing to the hindrance to the approach of the molecules, caused by the ortho-substituent. Or it may be due to a difference in constitution analogous to that indicated by Armstrong (Proc., 1892, 102).

L. M. J.

New Method for the Determination of the Density of Gases.

By HENRI MOISSAN and HENRI GAUTIER (*Ann. Chim. Phys.*, [7], 5, 568—573).—The principle made use of in this method is the same as that of the Dumas' vapour density method. The difference in weight between a given volume of gas, measured under given conditions of temperature and pressure, and the same volume of air measured under the same conditions is determined.

$$p = v \times 0.001293(x - 1) \times \frac{H}{760} \times \frac{1}{1 + 0.00367t}.$$

where p = difference between the two weights expressed in grams,

v = the volume of gas and of air,

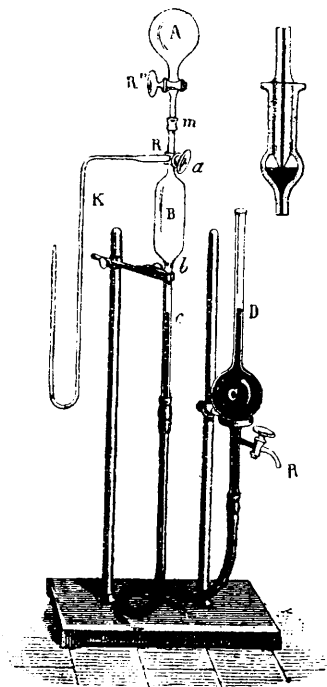
t = temperature and, H = pressure under which the volume is measured.

Then x = density of the gas.

The apparatus used is represented in the accompanying cut.

A is the globe in which the air or gas is weighed; it carries a three way cock, R'' and can be attached by means of an air-tight joint to the measuring vessel, B, which also has a three-way cock, R. K is a capillary tube, by which the gas to be investigated is introduced into B. The measuring vessel, B, is graduated on the stem bc , and has a capacity of about 95 c.c. The pressure is brought to the atmospheric by regulating the amount of mercury in D. The globe A is exhausted, and then filled with carefully dried air. This operation is repeated some 10 times, and then the cock R'' is turned off. B and K

are completely filled with dry mercury, and the point of K is then introduced into the vessel containing the gas to be examined, and



about 100 c.c. of gas are introduced into B, and the cock R is then turned, so as to shut off the measuring vessel from the rest of the apparatus, and the mercury in c and D is brought to the same level. The whole apparatus is then left for 6—7 hours, or still better over night, to attain a constant temperature. The temperature, volume, and pressure are then read, care being taken to see that the gas is at the atmospheric pressure. The cock R' is opened for a moment, in order that the air in A may assume the atmospheric pressure. A is then removed and weighed; it is afterwards exhausted, and again connected with B. The cocks R and R' are slowly opened, and the whole of the gas in B is made to pass into the globe, A, which is again detached, cleaned, and weighed.

The authors have determined the vapour densities of pure samples of carbonic anhydride, hydrogen, oxygen, and nitrogen, and they find that the numbers agree extremely well with those obtained by Regnault.

J. J. S.

Vapour Tension of Hydrated Salts and the Constitution of the Combined Water. By WILHELM MÜLLER-ERZBACH (*Zeit. physikal. Chem.*, 1896, **19**, 135—154).—The tension of aqueous vapour was determined, in the case of a number of hydrated salts, by finding the specific gravity of the sulphuric acid solution with which the salt remained in equilibrium, preliminary approximation being first made. The values for the vapour tension fall suddenly at definite changes of hydration for most salts, so that between certain limits of hydration the vapour tension remains constant. The results obtained were as follows, the vapour pressure being referred to that of water at the same temperature:—Barium chloride, 1—2 aq. 0.21, 0—1 aq. 0.10; copper sulphate, 3—5 aq. 0.31, 1—3 aq. 0.20; 0—1 aq. below 0.02; zinc sulphate, 6—7 aq. 0.55, 1—6 aq. 0.50, 0.1 aq. below 0.02; disodium hydrogen phosphate, 7—12 aq. 0.75, 3—7 aq. 0.58, 0—2 aq. 0.06.

L. M. J.

The Dilution Law for Salt Solutions. By FRIEDRICH KOHL-RAUSCH (*Zeit. physikal. Chem.*, 1895, **18**, 662).—Van't Hoff has shown that, according to Rudolphi's experiments, the expression C_i^3/C_s^2 leads to a constant value where C_i and C_s are the concentration of ions and undissociated compound (1895, ii, 490; this vol., ii, 145). This expression may be written $C_i/C_s = \text{const.}/C_s^{\frac{1}{2}}$, that is the ratio of the undissociated compound to ions is proportional to the linear density of the former.

L. M. J.

Partition of a Substance between Two Solvents. By A. A. JAKOWKIN (*Zeit. physikal. Chem.*, 1895, **18**, 585—594).—The partition coefficients were determined, in the case of solutions of iodine and bromine, in water and (1) carbon bisulphide, (2) bromoform, (3) carbon tetrachloride. In carbon bisulphide and water, a marked decrease of the partition ratio occurs with dilution, probably owing to the decomposition of complex molecules. A similar decrease occurs with bromoform, but with carbon tetrachloride the ratio remains almost constant. The numbers obtained with iodine for the carbon bisulphide-

ide: water ratio (685 to 600 at 18°) differ considerably from those obtained by Berthelot and Jungfleisch (400). In saturated solutions, the partition coefficient should be equal to the ratio of the solubilities in the two solvents, and the following table shows that this is the case, the numbers being obtained by extrapolation.

Water and	Solubility ratio.	Partition coefficient.
Carbon bisulphide.....	679·0	685·0
Bromoform	559·0	558·5
Carbon tetrachloride.....	89·6	89·7

On the assumption that the change in the coefficient is due to the passage from double to single molecules, the concentration of the aqueous solution is calculated from that in the other solvent, the numbers agreeing well with the observed values. The departure from normality in the case of solutions of carbonic anhydride is also considered and referred to the formation of complexes at the higher concentrations.
L. M. J.

The Course of Chemical Reactions in Gases. By LUDWIG STORCH (*Zeit. physikal. Chem.*, 1896, 19, 1—12).—According to the researches of van't Hoff, the reaction velocity for the formation of water from the mixed gases does not lead to a constant, if calculated for a trimolecular equation. The author, by applying the general differential equation $dC/dt = kC^n$, obtains a constant $k = 0\cdot004725$ when $n = 9$, in the case of moist mixed gases. For the experiments with the dry explosive mixture, the value obtained is $k = 0\cdot003091$; $n = 12$. It has also been shown that similar experiments with other gases do not lead to the reaction order expected, and the author explains these anomalies by the heat generated during the action. Thus, in the above case, at the temperature employed (boiling point of sulphur = 440°) the heat evolved per molecular equivalent is 111,345 units at constant volume, and 112,771 at constant pressure, so that the temperature of the water produced would be 3785° and 3108° respectively. At this temperature, however, the water molecules cannot exist, and in order that they may actually be formed, an excess of cooling molecules must be present. If 1500—2000° be taken as the temperature at which the water remains undissociated, the true equation hence becomes $(2H_2 + O_2 + 9\cdot8 M)_{440^\circ} = (2H_2O + 9\cdot8 M)_{1500^\circ}$, or $(2H_2 + O_2 + 4\cdot7 M)_{440^\circ} = (2H_2O + 4\cdot7 M)_{2000^\circ}$ at constant pressure, and similar equations occur with 12·9 M or 6·7 M at constant volume, so that the value for n should be between the limits 12·8—7·7 and 15·9—9·7 respectively. Similarly, the formation of hydrogen chloride should be abnormal, and the normal values of Bunsen and Roscoe are referred chiefly to the presence of the water, whilst the normal value of Bodenstein for the decomposition of hydrogen iodide, is owing to the fact that the thermal change accompanying it is very small (*Abstr.*, 1893, ii, 369; 1894, ii, 12).

L. M. J.

Chemical Kinetics of Oxidation. I. Speed of Liberation of Iodine in Mixed Solutions of Potassium Chlorate, Potassium Iodide, and Hydrochloric acid. By HERMAN SCHLUNDT (*Amer. Chem. J.*, **17**, 754—770).—Mixed solutions of potassium iodide and chlorate were heated at 100°, in small sealed tubes, with hydrobromic, hydrochloric, nitric, or sulphuric acid, the liberated iodine being estimated by titration with sodium thiosulphate. The conclusions drawn from the results are: (1) The speed of the reaction increases with the temperature. (2) Equivalent excess of iodide or chlorate produces equal accelerations, excess of acid produces a more marked acceleration. (3) The speed increases with the concentration. (4) For complete and rapid reduction of the chlorate, excess both of iodide and acid must be present. (5) The four common mineral acids may be arranged in the order given above, in regard to their relative influence in accelerating the action; the order being identical with that assigned to them by Ostwald.

A. L.

Chemical Kinetics of Oxidation. II. Mathematical Theory of Oxidation Processes. By ROBERT B. WARDER (*Amer. Chem. J.*, 1896, **18**, 23—43).—This paper is a review of the work which has been done in search of the mathematical law controlling the speed of oxidation of hydriodic acid in different systems, and has special reference to the preceding paper.

A. G. B.

Mixer for accelerating Chemical Reactions. By WLADIMIR MARKOWNIKOFF (*Annalen*, 1895, **289**, 254—257).—The author describes a form of apparatus which finds application to all classes of liquids, and may be heated or cooled, as occasion requires. Essentially it consists of a tinned copper cylinder capable of rapid rotation on its axis, and provided with ribs or beaters parallel to the axis.

M. O. F.

Pressure Tube for Laboratory Experiments. By JOHANN WALTER (*J. pr. Chem.*, 1896, [2], **53**, 132—139).—The object of this tube is to render it possible to maintain an external pressure on the glass tube which is being heated equivalent to the internal pressure, a principle which has been applied by Ullmann (*Ber.*, **23**, 379). The steel tube is of Mannesman make, and is of 32 mm. diameter, and 560 mm. in length. The head piece is usually of bronze, in which case no washer is necessary, the flange being tightened by a screw working in a stirrup, made in a piece with a collar welded on to the tube. Two side necks in the head-piece, provided with appropriate valves, permit of connection with a cylinder of compressed carbonic anhydride, and a manometer. In this way it is possible to maintain a constant pressure within the steel tube. The author finds that, instead of the usual pressure tubing, it is possible to use soft glass tubing of 1.5—2 mm. thickness in the walls when external pressure is maintained in this way, except when corrosive liquids are being heated; indeed, it is frequently permissible to omit to seal the glass tube, a cork serving when the carbonic anhydride is to be excluded and the temperature will permit. Details of the application of the tube for determining the solubility of sparingly soluble gases in

liquids, the solubility of substances at high temperatures under pressure, and the vapour pressure of liquids at high temperatures, are given, and two drawings accompany the paper.

A. G. B.

Inorganic Chemistry.

Nitrogen Sulphide. By A. CLEVER and WILHELM MUTHMANN (*Ber.*, 1896, **29**, 340—343).—Nitrogen sulphide, N_4S_4 , obtained by the action of ammonia on sulphur dichloride, yields bronze-coloured crystals of a compound, $N_4S_4Br_4$, when treated with bromine in carbon bisulphide solution; this decomposes in moist air, forming a yellow, amorphous compound, $N_4S_5Br_2$, or perhaps $N_4S_4SBr_2$. Nitrogen sulphide also absorbs bromine vapour, forming red crystals of the composition $N_4S_4Br_6$; this compound is very unstable; carbon bisulphide deprives it of some bromine, and it decomposes in moist air, yielding the compound $N_4S_5Br_2$. With nitric peroxide in carbon bisulphide solution, it yields crystals of a compound, NSO_4 , which is decomposed by water into nitric oxide and sulphuric acid. If the compound $N_4S_4Br_4$ is digested with nitric peroxide in carbon bisulphide solution, yellow crystals are formed, probably of the composition NSO ; these are very unstable, the heat of the hand being sufficient to decompose them. With nitric peroxide, the substance $N_4S_5Br_2$ forms large, yellow crystals of a compound, $N_4S_3O_6$. C. F. B.

Origin of the Argon and Helium in the Gas from Sulphuretted Waters. By LOUIS J. TROOST and LÉON V. R. OUVRARD (*Compt. rend.*, 1895, **121**, 798—799; and by BOUCHARD, *ibid.*, 800).—The gases extracted from the water of the Seine, and from sea water, contain argon, but only very feeble, and often uncertain, traces of helium. The gases from the sulphuretted waters of Caunterets, on the other hand, contain helium in distinct and readily recognisable quantities. The authors are of opinion that the helium is not derived from the atmosphere, but from minerals, such as cleveite, bruggerrite, monazite, &c., in the rocks through which the waters percolate.

BOUCHARD considers that although it may not be possible to attribute any special therapeutic action to the argon and helium present in the waters referred to, it is quite conceivable that compounds of them may be dissolved in the waters, and exert an important influence on their therapeutic effects. C. H. B.

Argon and Helium in a Mineral Water. By CHARLES MOUREU (*Compt. rend.*, 1895, **121**, 819—820).—Water from the spring at Maizières (Côte d'Or), which contains lithium compounds and very little calcium sulphate, was collected in such a way as to avoid contact with air, and the gas extracted from it was found to contain both argon and helium. The residue not absorbed by lithium at a dull red heat amounts to as much as from one-fifteenth to one-tenth of the total volume of the gas. C. H. B.

Separation of Atmospheric Argon and Nitrogen. By CLAUDIUS LIMB (*Compt. rend.*, 1895, 121, 887—888).—When barium fluoride or barium sodium fluoride (both of which can be obtained cheaply) is heated at a moderate temperature with sodium in an iron tube, a grey product is obtained, which consists chiefly of barium, and rapidly absorbs nitrogen. This process may probably be used for the separation of nitrogen from argon, although it is not yet definitely established that the latter is not absorbed by the barium. C. H. B.

Combination of Nitrogen with Metals of the Alkaline Earths. By LÉON MAQUENNE (*Compt. rend.*, 1895, 121, 1147—1148).—The author found some time ago that metals of the alkaline earths combine readily with nitrogen (*Abstr.*, 1892, 566 and 776), and this fact can be utilised for the isolation of argon, since either calcium or barium is readily obtained from its oxide by the action of magnesium. The most satisfactory results are obtained by means of a mixture of magnesium powder and pure and well dried calcium oxide heated at dull redness. C. H. B.

Combination of Nitrogen with Metals. By A. ROSSEL (*Compt. rend.*, 1895, 121, 941—943).—When powdered calcium carbide is mixed with magnesium powder and heated to dull redness in a crucible exposed to air, or in a tube through which air is passed, carbonic anhydride is liberated, and a mixture of calcium oxide and magnesium nitride is left. Aluminium, zinc, iron, and even copper, under similar conditions, yield similar products, which are decomposed by water with evolution of ammonia. C. H. B.

Absorption of Nitrogen by Lithium at the Ordinary Temperature. By HENRI DESLANDRES (*Compt. rend.*, 1895, 121, 886—887).—When lithium prepared by the Guntz method of electrolysis is heated in a vacuum, at a temperature a little below the softening point of glass, it gives off a notable quantity of hydrogen. The bright metal, when left in contact with nitrogen at the ordinary temperature, gradually and completely absorbs it, just in the same manner that phosphorus absorbs oxygen. The black film which forms on the surface of freshly cut lithium when exposed to the air, seems to prevent the absorption of the nitrogen, and in order to secure rapid and complete absorption, the bright surface of the lithium must be renewed from time to time. C. H. B.

Lithium Subchloride. By ANTOINE GUNTZ (*Compt. rend.*, 1895, 121, 945—947).—Lithium dissolves readily in fused lithium chloride, with formation of a new compound. If 27.4 grams of lithium chloride is heated to redness with 4.7 grams of lithium in a current of hydrogen, lithium subchloride, Li_2Cl , is obtained as a hard, greyish, homogeneous product, which decomposes water as readily as lithium does. $\text{Li}_2\text{Cl} + \text{H}_2\text{O} = \text{LiCl} + \text{LiOH} + \text{H}$. As a rule, the subchloride contains some nitrogen, but it seems to be free from the dark-coloured lithium nitride.

The author confirms the statements of previous observers as to the

readiness with which lithium combines with nitrogen on heating, and he finds that even when the air is not quite dry, a considerable quantity of nitride is formed at the ordinary temperature.

C. H. B.

Influence of Time on the Welding of Pressed Chalk. By WALTHER SPRING (*Zeit. anorg. Chem.*, 1896, **11**, 160—164).—The author has examined a cylinder of white, dry chalk which has been compressed in a steel press at 6000—7000 atmospheres for 17 years. The surface of the chalk cylinder, to a depth of $1-1\frac{1}{2}$ mm., was coloured yellow, owing to the diffusion of an iron compound, but the middle portion was quite white. It showed a conchoidal fracture similar to the fracture of lithographic stone; the middle portion was easily scratched with a needle, but the outside layer was very nearly as hard as marble, and gave indications of a crystalline structure.

This result shows that time has great influence on the welding of particles of a solid body when submitted to a pressure capable of bringing their surfaces into contact, and explains why the oldest rocks are generally the hardest and most solid.

E. C. R.

Action of Lead and of Potassium Nitrite on Lead Nitrate. By FRANZ PETERS (*Zeit. anorg. Chem.*, 1896, **11**, 116—159).—By the action of lead on an aqueous solution of lead nitrate, a basic lead nitrate, $\text{PbN}_2\text{O}_6, \text{PbO}_2\text{H}_2$, is first formed. When the ratio of lead to lead nitrate employed reaches 1:2 or 1: x where x is less than 2, isomorphous mixtures of basic lead nitrate with basic lead nitratonitrite, $\text{PbN}_2\text{O}_6, \text{PbN}_2\text{O}_4, 2\text{PbO}_2\text{H}_2$, are obtained. The latter is obtained alone when the ratio of lead to lead nitrate is 7:8 or 1:1. With gradually increasing proportions of lead, isomorphous mixtures of basic lead nitratonitrite with basic lead nitrite are obtained. With 1 of lead nitrate to $1\frac{1}{2}$ of lead, a dibasic lead nitratonitrite is formed. When the ratio of the lead is increased to $1\frac{3}{4}$ atoms, isomorphous mixtures of dibasic nitratonitrite with the tribasic nitrite,



are obtained; the latter alone is formed by the prolonged action of lead on a solution of lead nitrate. When $1\frac{1}{4}$ to $2\frac{1}{2}$ atoms of lead are employed to 1 vol. of lead nitrate, at first an isomorphous mixture of tribasic and monobasic nitrite is formed, and then dibasic nitrite, and from this an isomorphous mixture of the last salt with the tribasic nitrite. Lead oxide can be employed in place of lead in order to convert one of the salts of this series into another containing a larger proportion of lead oxide.

When a solution of potassium nitrite is allowed to act on a boiling solution of lead nitrate, a basic lead nitrate is at first formed as is the case when the lead nitrate is treated with metallic lead. It is obtained by employing the reagents in the ratio $\text{PbN}_2\text{O}_6 : \text{KNO}_2 = 1 : 1$ to $3 : 4$. When the ratio reaches 2:3 or 1:2 basic lead nitratonitrite, $\text{PbN}_2\text{O}_6, \text{PbN}_2\text{O}_4, 2\text{PbO}_2\text{H}_2, 2\text{H}_2\text{O}$ is formed. By increasing the proportion of potassium nitrite, the compounds described above are obtained. As the action of potassium nitrite on lead nitrate is similar to that of lead, so also it converts the first members of the series of

compounds obtained by the action of lead into the following members of the series.

E. C. R.

Action of Alcohol on Mercurous Iodide. By MAURICE FRANÇOIS (*Compt. rend.*, 1895, **121**, 888—891).—Although alcohol is commonly employed in the preparation of mercurous iodide, it is not without action on it, especially when heated. Boiling alcohol decomposes the iodide into mercuric iodide and mercury, the action being limited and reversible, and the decomposition ceasing when the boiling alcohol of 95° contains 0.222 gram of mercuric iodide in 100 grams of the liquid. With a higher proportion, the solution acts on mercury and converts it into mercurous iodide until the limit is reached. 1000 grams of boiling alcohol of 95° will decompose about 3.15 grams of mercurous iodide; the alcohol commonly employed for washing mercurous iodide gradually decomposes it, removing mercuric iodide and leaving mercury; and the two iodides cannot be accurately separated by means of alcohol.

C. H. B.

Presence of Sodium in Aluminium prepared by Electrolysis. By HENRI MOISSAN (*Compt. rend.*, 1895, **121**, 794—798).—Many specimens of aluminium, prepared by electrolysis, contain small quantities of sodium, the presence of which can sometimes be made evident by allowing the metal to remain for a long time in contact with water, especially if the liquid is boiled from time to time. In the specimens examined, the proportion of sodium varied from 0.1 to 0.3 per cent. An old specimen contained 0.42 per cent. When sodium is present, the aluminium is attacked by cold water, and if the water is not changed, the action increases in rapidity owing to the formation of sodium aluminate, which is dissociated by the water with continual regeneration of sodium hydroxide. Small quantities of sodium will also have an important influence on the properties of alloys of aluminium with other metals. Riche found that an alloy of aluminium and tin is attacked by cold water, and the author confirms this statement, even when the aluminium is free from sodium.

Many alloys of aluminium with other metals are attacked by water or saline solutions, and the chief reason seems to be that as a rule they are not homogeneous, and small galvanic circuits are formed at the surface of the metal. On the other hand, if the metal is homogeneous and is free from nitrogen, carbon, and sodium, it is not affected by water. The great tendency that aluminium shows to form galvanic couples with other metals indicates that, for constructive purposes, it should always be used alone in as pure a form as possible, and not alloyed with another metal, nor should it be in contact with other metals.

C. H. B.

Combination of Anhydrous Ammonia and Aluminium Chloride. By JOHN M. STILLMAN and MINNIE B. YODER (*Amer. Chem. J.*, 1895, **17**, 748—753).—Carefully dried ammonia, at first mixed with air in order to mitigate the violence of the action, is passed over cooled, anhydrous aluminium chloride. The product, $\text{AlCl}_3 \cdot 6\text{NH}_3$, is a bulky, white powder with a powerful odour of ammonia. It is decomposed by water, with production of aluminium hydroxide.

When heated in a current of dry air, it undergoes oxidation, a compound of alumina and ammonium chloride being formed. The former substance, when heated in dry hydrogen, yields a hygroscopic compound, $\text{AlCl}_3 \cdot 2\text{NH}_3$. These results are similar to those obtained in the case of ferric chloride.

The compound, $\text{AlCl}_3 \cdot 3\text{NH}_3$, described by Rose and by Persoz (see Graham Otto, 5 *Auf.*, 4, 2, 31), was not obtained. A. L.

Action of Ferric Salts on Iodides in Aqueous Solution. By FRIEDRICH W. KÜSTER (*Zeit. anorg. Chem.*, 1896, 11, 165—174).—A theoretical paper in which the author discusses the results obtained by Seubert (*Abstr.*, 1895, ii, 17, 111, and 395). These results are in accordance with Arrhenius's theory and its consequences.

E. C. R.

Silicides of Iron. By GUILLAME DE CHALMOT (*J. Amer. Chem. Soc.*, 1895, 17, 923—924).—By heating a mixture of iron filings, sand, and charcoal in an electric furnace, the author obtained a silicide containing 23—27 per cent. of silicon. Occasionally it forms crystals about 1 cm. long of a pure ferric silicide of the formula Fe_3Si_2 . It is white and crystalline, of sp. gr. = 6.36, hard, brittle, and only slightly magnetic, but is a good conductor of electricity. It is fairly proof against oxidising acids, but is slowly attacked by cold nitro-hydrochloric acid (1 : 3), which, however, chiefly dissolves the iron, but scarcely any silicon. Fusion with potassium nitrate and potassium sodium carbonate, or treatment with hydrofluoric acid soon breaks up the compound.

The author also obtained a compound approaching the formula FeSi_2 , which had a sp. gr. of 4.851, was non-magnetic, and was scarcely acted on by aqua regia. L. DE K.

Atomic Weight of Cobalt. By WALTHER HEMPEL and HERMANN THIELE (*Zeit. anorg. Chem.*, 1896, 11, 73—105).—The authors have re-examined the methods of determining the atomic weight of cobalt employed by Remmler (*Abstr.*, 1893, ii, 211) and C. Winkler (*Abstr.*, 1893, ii, 469).

The material employed was prepared by fractionally precipitating 3 kilos. of cobalt chloride with a solution of potassium hydroxide; 22 fractions were obtained. The results obtained with separate fractions, according to Remmler's method, show that the experimental errors are much greater than the difference in the atomic weight.

Method by Reduction of the Oxide Co_3O_4 .—The pure material was prepared as follows: Each fraction was treated (1) with hydrogen sulphide; (2) twice precipitated with potassium nitrite to separate it from nickel; (3) precipitated with ammonia to remove alumina, ferric oxide, and silica; (4) twice precipitated with ammonium sulphide, and washed with hydrochloric acid to remove alkali and traces of iron and zinc, the oxide obtained by roasting the sulphide was then reduced, washed with water, dissolved in nitric acid, and the nitrate cautiously decomposed by heating in a platinum basin. The oxide thus obtained is heated to a constant weight in a current of carbonic

anhydride or nitrogen, and then reduced in a current of hydrogen. The mean of three experiments gave the atomic weight $\text{Co} = 58.848$.

A second and third series of determinations were made according to Winkler's method by taking a known weight of metal, converting it into chloride, and precipitating with silver nitrate, the weight of cobalt chloride and of silver chloride being determined. A special apparatus, by which all errors due to dust, moisture, &c., were eliminated as nearly as possible, was employed, drawings of which are given in the original paper. A weighed quantity of the metal, purified by electrolytic decomposition, was dissolved in hydrochloric acid, evaporated to dryness, and heated in a current of hydrogen chloride at 195° until the weight became constant. After the hydrogen chloride had been removed by a current of carbonic anhydride while the apparatus was still hot, and then the carbonic anhydride by means of an air-pump, the cobalt chloride was weighed, and the chlorine estimated gravimetrically. The mean of six experiments in which the cobalt chloride was weighed gave $\text{Co} = 58.64$, and the mean of four experiments in which the silver chloride was weighed gave $\text{Co} = 58.770$. The mean values obtained, corrected to vacuum, were (1) by weighing the oxide and metal, $\text{Co} = 58.826$, (2) by weighing the metal and chloride, $\text{Co} = 58.61$, (3) by weighing the metal and silver chloride, $\text{Co} = 58.765$; when $\text{O} = 15.96$, $\text{Cl} = 35.37$, and $\text{Ag} = 107.66$. The last value is probably the most accurate. E. C. R.

Action of Hypochlorous acid on the Chlorides of Cobalt and Manganese. By EUTHYME KLIMENKO and BORIS KLIMENKO (*Ber.*, 1896, **29**, 478—481).—The authors have estimated the amount of the oxides of manganese and cobalt which are precipitated when solutions of the corresponding chlorides and of hypochlorous acid are mixed. Their results show that the maximum amount of manganese peroxide is precipitated when the ratio of the amounts of the two reagents is that theoretically required for the production of MnO_2 . In the case of the cobalt compound, the relative amount of the sesquioxide produced does not appear to be materially diminished when the relative amount of hypochlorous acid is diminished to one-third of that theoretically required for the production of Co_2O_3 . A. H.

Chromium Amalgam and some Properties of Chromium. By JULES FÉRÉE (*Compt. rend.*, 1895, **121**, 822—824).—Experiments previously made by the action of sodium amalgam on haloïd chromium salts, or by the electrolysis of chromium salts in presence of mercury, have yielded amalgams containing only a very small proportion of chromium. The author finds that better results are obtained by electrolysing a solution containing 160 grams of chromic chloride and 100 grams of concentrated hydrochloric acid in 740 grams of water by means of a powerful current with a mercury cathode and a platinum anode. Using a current of 22 ampères and a mercury surface of 8.05 sq.c. he obtained 1.5 kilo. of a solid chromium amalgam; when dried and filtered through chamois leather, the amalgam has the composition Hg_3Cr . When this is subjected to a pressure of 200 kilos. per sq.c., it loses mercury and yields another amalgam of

the composition HgCr . The first amalgam is soft, brilliant, and alters but little in air, but when heated loses mercury without melting and oxidises rapidly; the second is brilliant and harder, but alters more readily. When distilled in a vacuum below 300° , they both yield chromium which is pyrophoric at ordinary temperatures, and combines with both oxygen and nitrogen, the whole mass being raised to a bright red heat. At the ordinary temperature, it absorbs nitric oxide with incandescence and the production of a mixture of chromium nitride and oxide, and it also absorbs nitrogen, becoming incandescent and forming chromium nitride. When heated more strongly in a vacuum, the pyrophoric chromium loses its activity.

C. H. B.

Crystallised Chromous Sulphide. By A. MOURLOT (*Compt. rend.*, 1895, **121**, 943—945).—Chromous sulphide, CrS , is obtained by passing hydrogen sulphide over chromium, heated at the highest temperature of a coke reverberatory furnace, or in the electric tube furnace. In the latter, it fuses, and, when cooled, has a crystalline structure, and contains cavities lined with prismatic needles which scratch quartz easily. Its sp. gr. is 4.08. Fluorine attacks it at incipient redness, chlorine at about 340° , bromine at a higher temperature, and iodine not at all. It burns readily in oxygen, and is attacked by hydrogen fluoride in the cold, but by hydrogen chloride only at a bright red heat. Concentrated acids attack it either in the cold or on heating gently, and this is true of potassium chlorate or nitrate and lead peroxide. Fused alkali carbonates oxidise the sulphide. Hydrogen does not attack chromous sulphide at 1200° , but carbon reduces it in the electric furnace.

C. H. B.

Titanium Silicide and Crystallised Titanium. By LUCIEN LÉVY (*Compt. rend.*, 1895, **121**, 1148—1150).—The action of titanium chloride on silicon at a high temperature yields arborescent crystals, the composition of which corresponds with the formula Ti_2Si . Whether they are identical with the crystals previously described (*Abstr.*, 1890, 1066) is not yet ascertained. There is reason to believe that in many cases the crystalline products of the action of titanium chloride on metals, silicon, &c., contain crystals of titanium.

C. H. B.

Alums of Vanadium Trioxide. By AUGUSTO PICCINI (*Zeit. anorg. Chem.*, 1896, **11**, 106—115).—*Ammonium vanadium alum*, $\text{NH}_4\text{V}(\text{SO}_4)_2 + 12\text{H}_2\text{O}$, is obtained by treating ammonium metavanadate mixed with sulphuric acid with a saturated solution of sulphurous anhydride until all the salt is dissolved. The solution is heated on the water-bath until the sulphurous anhydride is eliminated, and then reduced by means of an electric current. It crystallises in pentagonal hemihedral forms belonging to the cubic system, and is violet. It is very easily soluble in water, and the crystals, on exposure to air, become gradually covered with a pale green skin. At 50° , it melts in its water of crystallisation to a green liquid, which then solidifies to a green mass, changing to violet; at 230° , it is converted into an anhydrous, yellowish-green mass, which is not

completely soluble in water, but gradually dissolves on exposure to air forming a blue solution. When heated above 300° , it is decomposed, with formation of vanadic anhydride.

The author was unable to prepare a vanadium alum with hydroxylamine sulphate. By working in a similar manner to the above, a small quantity of the ammonium salt was obtained. The vanadium trioxide is oxidised by hydroxylamine, according to the equation $V_2O_3 + NH_3O = V_2O_4 + NH_3$. The sesquioxides of titanium and molybdenum are also converted into the dioxides when treated with hydroxylamine.

Rubidium vanadium alum, $RbV(SO_4)_2 + 12H_2O$, is obtained in a similar manner to the ammonium salt. It crystallises in transparent, bluish-violet, hemihedral forms belonging to the cubic system, and is much less soluble than the ammonium salt. It gradually gives up its water at 100° , and turns yellowish-green, is anhydrous at 230° , and is then no longer soluble in water; when heated above 300° , it is decomposed.

Cæsium vanadium alum, obtained in a similar manner, crystallises in ruby-red to amethyst-violet cubical crystals, and is very sparingly soluble in cold water, but much more readily in hot water. The crystals are only slightly altered by exposure to air, gradually give up water at 100° , are anhydrous at 230° , and then turn green, and are decomposed when heated above 300° . E. C. R.

Existence of Sulphoxyantimonates. By LEROY W. MCCAY (*Amer. Chem. J.*, **17**, 770—778).—The salt obtained by Rammelsberg (*Ann. Phys. Chem.*, 1841) by the action of potassium hydroxide on antimony pentasulphide, is not a double salt, but a secondary potassium orthosulphoxyantimonate, $K_2HSbO_2S_2 + 2H_2O$. It is prepared by allowing a cold solution of potassium hydroxide to act on antimony pentasulphide during 24 hours. It crystallises in radiating clusters of needles, which in moist air assume a red or crimson colour, without deliquescing. At 150° , it loses $2H_2O$, a temperature of 250° being necessary to expel the combined water. Aqueous solutions of the salt give, with metals of the alkaline earths, white precipitates which become crystalline; with silver salts, a black precipitate; and with copper and lead salts, red precipitates which gradually turn black. Hydrochloric acid decomposes the salt with formation of antimony tri-, and penta-sulphides, tri- and pent-oxides, and sulphur.

A. L.

Derivatives of Niobium and Tantalum. By MARY E. PENNINGTON (*J. Amer. Chem. Soc.*, 1896, **18**, 38—67).—The decomposition of columbite when fused with potassium acid sulphate is not quite so rapid or complete as by the method proposed by Gibbs, who decomposes the mineral by fusing with potassium hydrogen fluoride. When the double fluorides thus obtained are submitted to the action of the electric current, a lower hydrated oxide of niobium and tantalum is incompletely precipitated. The hope of discovering a better method for the separation of niobium, tantalum, and titanium by the difference in the solubility of their double fluorides with rubidium and cæsium has not been realised. The heating of the oxides of niobium

and tantalum in sealed and vacuous tubes with phosphorus pentachloride yields their pentachlorides and phosphorus oxychloride.

The authoress communicates a delicate reaction for niobium, applicable to any soluble compound. An excess of potassium thiocyanate is added to the dissolved substance, and then some pieces of zinc, followed by strong hydrochloric acid. The solution becomes at once a bright golden-brown, or, if much niobium is present, almost red; the colour is stable for about 24 hours, and is not altered by a brisk and continuous evolution of the gas; tantalum and titanium do not give this reaction. Admixture of titanium may be proved by the following test. A few c.c. of strong sulphurous acid is treated in a test tube with a few pieces of zinc; as soon as evolution of gas ceases, the liquid is added to the solution to be tested; a solution containing titanium at once gives an orange-yellow coloration; columbium or tantalum yields, after some time, a white precipitate. Many other tests are given.

L. DE K.

Mixed Haloïd Compounds of Platinum and Potassium. By CHARLES H. HERTY (*Ber.*, 1896, **29**, 411—414).—The series of compounds, $K_2PtCl_nBr_{6-n}$ (n less than 5), prepared by Pitkin (*J. Amer. Chem. Soc.*, **1**, 472; **2**, 196), is shown to consist of isomorphous mixtures, in different proportions, of the two salts, K_2PtCl_6 and K_2PtBr_6 .

C. F. B.

Mineralogical Chemistry.

Phosphorescent Diamonds. By GEORGE F. KUNZ (*Trans. New York Acad. Sci.*, 1895, **14**, 260).—The various colours of diamonds are attributed to the presence of hydrocarbons, and the phosphorescence and fluorescence of certain diamonds are attributed to a bluish-white substance, which is undoubtedly a hydrocarbon, and for which the name *tiffanyite* is proposed.

L. J. S.

Artificial Formation of Magnetic Pyrites [Pyrrhotite]. By L. BUCCA (*Zeit. Kryst. Min.*, 1895, **25**, 398; from *Rivista Min. Crist.*, 1893, **13**, 10).—A luting, consisting of a mixture of sulphur, iron filings, and ammonium chloride, used for mending broken retorts in the sulphur industry in Catania, Sicily, was found, after having been heated for several months, to consist essentially of FeS . In cavities in this mass were tabular crystals of hexagonal outline; these had the sp. gr. 4.545, and contained 41.4 per cent. of sulphur, corresponding with the formula Fe_4S_5 . It is supposed that pyrrhotite may be represented by the formula $n\text{FeS} + \text{Fe}_3\text{S}_4$, and the strong magnetic character of the present crystals is supposed to be due to the near approach of Fe_4S_5 to Fe_3S_4 .

L. J. S.

Plumboferrite from Sjö Mine, Sweden. By LARS J. IJELSTRÖM (*Jahrb. f. Min.*, 1896, i, Ref. 15; from *Geol. För. Förh.*, 1894, 16, 594).—Plumboferrite, before only known from Jakobsberg, Sweden, has been found at the Sjö mine, Örebro, as hexagonal plates having the appearance of molybdenite; streak, pale red. After deducting much admixed barytes, and calculating the FeO in agreement with the formula $(\text{Pb,Fe,Cu})\text{O,Fe}_2\text{O}_3$, the analysis is given as

Fe_2O_3 .	PbO.	FeO.	CuO.	Total.
54·67	32·60	9·21	3·52	100·00

L. J. S.

New Method of producing Artificial Oligiste [Hæmatite]. By HENRYK ARCTOWSKI (*Bull. Acad. Belg.*, 1894, [3], 27, 933—936).—On passing a rapid current of ammonium chloride vapour over ferric oxide heated at about 700° , small crystals of hæmatite are formed. This is a modification of previous methods; hydrogen chloride being supplied by the dissociation of the ammonium chloride, the water vapour and ferric chloride thus formed reacting to form crystallised hæmatite. At lower temperatures, the ammonium chloride is absorbed by the ferric oxide, and ferric chloride alone formed. Fine, unmodified cubes of ammonium chloride are deposited with the hæmatite. As ammonium chloride is found in volcanic fumaroles, it is suggested that it may have aided in this way in the formation of hæmatite.

L. J. S.

Artificial Cassiterite. By ANDREAS ARZRUNI (*Zeit. Kryst. Min.*, 1895, 25, 467—470).—Cassiterite, formed by the oxidation of tin vapour, or by the deposition of tin oxide from molten tin, occurs in druses in a refractory furnace material. The distorted, prismatic crystals, which measure up to 1 cm. by $\frac{1}{2}$ cm., are brown or light violet in colour, the latter being transparent, and dichroic; there are no twin crystals. Measurements of the crystal angles, and of the indices of refraction are given.

	Li.	Na.	Tl.
w	1·9846	1·9968	2·0093
ϵ	2·0817	2·0929	2·1053

With these crystals, there is a red-brown or green, granular tin dioxide; and also tin dioxide in the form of long, delicate, colourless needles, giving optical extinction angles of 0 — 19° , and being apparently monosymmetric.

L. J. S.

Nickel Ore [Gersdorffite] from the Upper Harz. By FRIEDRICH KLOCKMANN (*Jahrb. f. Min.*, 1896, i, Ref. 63; from *Zeit. prakt. Geol.*, 1893, 1, 385).—In the Gross-Schleifsteinthal, south of Goslar, there has recently been found a lode of nickel ore, consisting principally of gersdorffite, with also pyrites and calcite. Analyses by G. Bodländer gave I for the crystals, and II for the massive ore.

	Ni.	Co.	Fe.	As.	Sb.	S.	Insol.	Total.
I. 32·65	1·00	0·60	45·20	1·96	17·75	0·95		100·11
II. 30·15	1·34	0·84	43·87	1·55	16·09	5·61		99·45

L. J. S.

Rhodophosphite and Tetragophosphite, two new Minerals from Horrsjöberg, Wermland. By LARS J. IGELSTRÖM (*Zeit. Kryst. Min.*, 1895, **25**, 433—436).—*Rhodophosphite* occurs as white to pale red, hexagonal prisms, translucent to opaque, along with lazulite, kyanite, damourite, ilmenite, svanbergite, manganiferous garnet, &c., in quartzite, at Horrsjöberg, Wermland, Sweden. Analyses gave

P ₂ O ₅ .	CaO.	MnO + FeO.	Cl.	SO ₃ .	F.	Total.
36.42	45.17	8.80	2.92	1.34	not estim.	97.93

Considering the difference as fluorine, the formula is deduced as $20(\text{RO})_3\text{P}_2\text{O}_5 + 4(\text{CaCl}_2, \text{CaF}_2) + \text{CaO}, \text{SO}_3$. In containing sulphuric acid, which seems to be always present in constant amount, the mineral resembles svanbergite, and differs from apatite, with the latter of which it is sometimes intergrown.

Tetragophosphite occurs at the same locality with rhodophosphite, as transparent, four-sided blue plates; it is not attacked by acids; analyses gave

P ₂ O ₅ .	Al ₂ O ₃ .	FeO + MnO.	MgO + CaO.	H ₂ O.	Total.
36.92	40.00	9.51	7.50	5.96	100.00
33.64	41.81	9.51	6.74	8.30	100.00

Formula, $(\text{RO})_3\text{P}_2\text{O}_5 + (\text{Al}_2\text{O}_3)\text{P}_2\text{O}_5 + 3\text{H}_2\text{O}$; this is slightly more basic than lazulite; it is near to the "light blue phosphate" of Blomstrand (1868), from Westanå, Skåne, Sweden, where similar phosphates to those of Horrsjöberg occur.

L. J. S.

[**Columbite from Wakefield, New Hampshire.**] By MARY ENGLE PENNINGTON (*J. Amer. Chem. Soc.*, 1896, **18**, 39—45).—Occurs in large, black, lustreless masses; sp. gr. = 5.662 at 4°. Small, bright yellow patches of uraconite are scattered over the surface. Analysis gave

Ta ₂ O ₅ .	Nb ₂ O ₅ .	TiO ₂ .	WO ₃ .	SnO ₂ .	U ₃ O ₈ .	Fe ₂ O ₃ .	FeO.	CaO.	MnO.	H ₂ O.	Total.
78.04			0.24	0.48	5.22	6.42	0.02	8.96	1.22	100.6	

A. J. G.

Inesite from Jakobsberg, Sweden. By AXEL HAMBERG (*Jahrb. f. Min.*, 1896, i, Ref. 20; from *Geol. För. Förh.*, 1894, **16**, 304).—Rose-coloured inesite has been found with kentrolite and calcite in a granular limestone at Jakobsberg, Nordmark. The triclinic crystals are tabular parallel to (100), and show the cleavages (010) perfect, (100) distinct, (110) imperfect. Analysis gave

SiO ₂ .	PbO.	MnO.	MgO.	CaO.	H ₂ O (over H ₂ SO ₄).	H ₂ O (on ignition).	Total.
42.92	0.73	36.31	0.37	8.68	0.62	9.86	99.49

The fine powder absorbed 2.7 per cent. of water in a damp atmosphere, but this was again lost (with 0.62 per cent. in addition) in the desiccator. After being dried over sulphuric acid, there is a loss of 1.09 per cent. H₂O at 53°, of 2.14 per cent. at 100°, and of 4.39 per cent. at 200°. The formula is given as $(\text{Mn}, \text{Ca})\text{H}_2\text{SiO}_4$ or $(\text{Mn}, \text{Ca})\text{SiO}_3 + \text{H}_2\text{O}$; this, however, requires 12.5 per cent. of H₂O.

L. J. S.

Forsterite from Monte Somma. By ANDREAS ARZRUNI (*Zeit. Kryst. Min.*, 1895, **25**, 471—476).—Measurements of the crystal angles and of the optic axial angles are given for colourless, transparent crystals of forsterite from the bombs of Mte. Somma.

$$a : b : c = 0.46663 : 1 : 0.58677 \text{ (S. Jolles).}$$

The crystals are thick, tabular parallel to $b(010)$, and are sometimes twinned on both $h(011)$ and (031) . Analyses by K. Thaddéeff on two samples gave

	SiO ₂ .	MgO.	FeO.	CaO.	Al ₂ O ₃ .	Total.	Sp. gr.
I.	42.65	56.57	1.35	0.29	—	100.86	3.223
II.	42.39	55.09	3.12	—	0.23	100.83	3.245

Deducting lime from I as belonging to calcite or wollastonite, and alumina and the corresponding amount of monoxides to form pleonaste from II, these analyses reduce very closely to $2\text{RO}, \text{SiO}_2$.

L. J. S.

Guarinite. By ORAZIO REBUFFAT (*Jahrb. f. Min.*, 1896, i, Ref. 28; from *Lab. chim. R. scuola di app. gl'ingegneri, Napoli*, 1894, 1—10).—From the incomplete analysis previously made of this Vesuvian mineral, it has been considered to be a titano-silicate of calcium; the following analysis is now given.

SiO ₂ .	Y ₂ O ₃ ?	Ce ₂ O ₃ .	Fe ₂ O ₃ .	Al ₂ O ₃ (diff.).	CaO.	Na ₂ O.	K ₂ O.	Total.
34.84	1.23	3.45	1.69	25.37	25.20	6.57	1.56	99.91

This gives the formula $10\text{SiO}_2, 5(\text{Al}, \text{Fe}, \text{Ce})_2\text{O}_3, 8\text{CaO}, 2(\text{Na}, \text{K})_2\text{O}$. This is the first Vesuvian mineral in which cerium has been found.

L. J. S.

Caswellite, an altered Biotite from Franklin Furnace, N.J. By ALBERT H. CHESTER (*Trans. New York Acad. Sci.*, 1894, **13**, 181—183).—This new mineral, from Trotter mine, Franklin Furnace, N. J., which has the characters of a clintonite, is flesh-red to light copper-red; it has a bronzy lustre, a micaceous structure, and is brittle; $H = 2.5\text{—}3$; sp. gr. = 3.54. It is associated with massive, yellow garnet (polyadelphite), rhodonite, and somewhat altered, dark brown biotite, into the latter of which there is a gradual passage. It is completely decomposed by hydrochloric acid, with separation of gelatinous silica; the mean of two analyses is

Loss on ignition.	SiO ₂ .	Fe ₂ O ₃ .	Al ₂ O ₃ .	Mn ₂ O ₃ .	CaO.	MgO.	Total.
4.64	38.74	6.85	6.58	15.95	22.30	2.52	100.58

This gives approximately the ratio $\text{SiO}_2 : \text{R}_2\text{O}_3 : \text{RO} : \text{H}_2\text{O} = 6 : 2 : 5 : 2.5$. The mineral is very feebly doubly refracting, has no pleochroism, and has a larger optic axial angle than the biotite from which it has been derived. Unaltered biotite from another part of the mine contains a considerable amount of potassium, much magnesium, and little or no calcium, and it is supposed that the caswellite has been derived by the local action of water containing manganese and calcium on this biotite, the alkalis having been carried away.

L. J. S.

Andalusite and Spessartite from Bodenmais, Bavaria. By ERNST WEINSCHENK (*Zeit. Kryst. Min.*, 1895, **25**, 357—364).—*Andalusite*.—This occurs as unaltered, prismatic crystals in the pyrrhotite deposits of Silberberg, near Bodenmais, together with quartz, orthoclase, biotite, cordierite, &c. When enclosed in the quartz, it is clear and transparent, greenish to reddish in colour, and strongly pleochroic; but when embedded in the pyrrhotite, it is dark in colour, owing to enclosures of this mineral.

Spessartite.—This garnet lines fissures in a cordierite-gneiss at the same locality; dodecahedral crystals rest on a layer of the massive mineral, and the remainder of the fissure is filled up with pyrrhotite, pyrites, and blende. Analysis gave

SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	FeO.	MnO.	CaO.	Total.
34.65	20.00	2.55	9.17	33.87	trace	100.24

The FeO is calculated by means of the garnet formula from 12.72 per cent. Fe₂O₃, which represents the total iron. A section shows a regular division into optically biaxial fields. The Aschaffenburg spessartite, of much the same composition, occurs as a primary constituent in granite, and differs in optical characters.

Tourmaline from Zwiesel and manganapatite from near Bodenmais are described, and cacoenite is mentioned as an alteration product of the Rabenstein triphylite.

L. J. S.

Crystalline form of Riebeckite. By WILLIAM J. SOLLAS (*Proc. Roy. Irish Acad.*, 1895, [3], **3**, 516—523).—A micro-granite in the glacial deposits of the east coast of Ireland, and probably derived from Ailsa Craig, in the Firth of Clyde, contains, in drusy cavities, crystals of quartz, felspar, and riebeckite. The latter gave the crystallographic constants, $a : b : c = 0.54748 : 1 : 0.29246$; $\beta = 76^\circ 10'$, which have not been before determined for this variety of hornblende. A partial analysis gave

SiO ₂ .	Al ₂ O ₃ , Fe ₂ O ₃ .	Na ₂ O.	K ₂ O.
42.69	41.71	10.00	0.87

L. J. S.

Jadeite from "Tibet." By MAX BAUER (*Jahrb. f. Min.*, 1896, i, 85—95).—Amongst jadeite pebbles from "Tibet in N. Himalayas," four colour varieties are distinguished: (1) snow-white with a tinge of lilac or violet; (2) white with a tinge of grey; (3) white with a greenish tinge; (4) sombre green with blue and grey shades, the green colour being here due to iron and not to chromium, as in the emerald green spots of the white varieties. The last variety consists of interwoven needles and fibres, sp. gr. = 3.325, and contains veins and strings of white, compact, granular nepheline, which, on analysis by K. Busz, gave

SiO ₂ .	Al ₂ O ₃ .	CaO.	Na ₂ O.	K ₂ O.	H ₂ O.	Total.	Sp. gr.
42.47	35.92	1.02	14.57	4.27	2.39	100.64	2.628

With this is a small quantity of basic plagioclase, and enclosed in the nepheline grains are needles and prisms of jadeite. There is here,

therefore, a jadeite-plagioclase-nepheline rock, in which nepheline plays the part of the ground-mass, and in which, locally, the relative amounts of the constituents vary very considerably, the larger green portion consisting mainly of jadeite, with here and there only a little felspar and nepheline. Two of the white varieties also show a little of this felspar and nepheline. Nepheline has previously only been recorded in igneous rocks, and its occurrence as a constituent of a crystalline schist is new. The low sp. gr. given for some jadeites (sometimes below 3, the normal being 3.3) is explained better by the presence of these minerals than by assuming uraltisation, for, if the whole of the pyroxene were changed to hornblende, the sp. gr. would still be greater than 3. This, together with isomorphous replacement, also explains the variations in chemical composition. L. J. S.

Jadeite from Mogoung, Burma. By OLIVER C. FARRINGTON (*Jahrb. f. Min.*, 1896, i, Ref. 19—20; from *Proc. U.S. National Museum*, 1894, 17, 29—31).—Translucent, finely granular, white jadeite, from the Uru valley, gave the following result, which is the mean of two analyses on the white portion, the pale green spots being neglected.

SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	CaO.	MgO.	MnO.	Na ₂ O.	Loss on ignition.	Total.
59.22	24.55	0.34	0.18	trace	trace?	14.46	1.14	99.89

This comes near to pure Na₂O, Al₂O₃, 4SiO₂. When examined under the microscope, minute grains and fibres are seen, having the optical characters of pyroxene, and, in places, commencing alteration to hornblende. L. J. S.

Jadeite, Albite, and Glaucophane from Tammaw, Upper Burma. By MAX BAUER (*Records Geol. Survey, India*, 1895, 28, 91—105; and *Jahrb. f. Min.*, 1896, i, 18—51).—*Jadeite*.—This is snow-white with emerald-green spots, the latter containing chromium; sp. gr. varies from 3.338 to 3.325. Under the microscope, it is seen to consist of an aggregate of irregular pyroxene prisms. Analysis by K. Busz gave

SiO ₂ .	Al ₂ O ₃ .	CaO.	MgO.	Na ₂ O.	Loss on ignition.	Total.	Sp. gr.
58.46	25.75	0.63	0.34	13.93	1.00	100.11	3.332

Chromium and iron are absent. This corresponds with 90.1 per cent. of Na₂O, Al₂O₃, 4SiO₂, 4.59 of MgO, Al₂O₃, 4SiO₂, and 1.28 of CaO, SiO₂.

Albite.—Analysis by K. Busz of the snow-white ground-mass of an albite-hornblende rock gave

SiO ₂ .	Al ₂ O ₃ .	CaO.	MgO.	K ₂ O.	Na ₂ O.	Total.	Sp. gr.
64.60	19.92	trace	trace	1.02	14.01	99.55	2.587

This includes small quantities of augite, rhombic pyroxene, and an undetermined mineral.

Glaucophane.—This, as large, greyish crystals, forms the main part of an emerald-green glaucophane-schist; the green colour being due

to crystals of bright green augite containing chromium; the augite enclosed in the glaucophane was not separated for the following analysis, by K. Busz; sp. gr. = 3.113—3.126.

SiO ₂ .	Al ₂ O ₃ .	Cr ₂ O ₃ .	FeO.	CaO.	MgO.	Na ₂ O, K ₂ O.	Loss on ignition.	Total.
53.53	9.10	4.02	6.94	15.94	7.96	2.95		100.44

The large amount of soda in this amphibole points to glaucophane, although the optical characters are somewhat unusual. L. J. S.

Epidote from the Harz. By OTTO LÜDECKE (*Jahrb. f. Min.*, 1896, i, Ref. 30; from *Abhandl. Ges. Halle*, 1894, 20, 311—325).—In cavities of a tourmaline granite on Ramberg are crystals of smoky quartz, epidote, tourmaline, fluorite, albite, orthoclase, zoisite, and apatite, of which crystallographic descriptions are given. The minerals are supposed to have originated in the decomposition of the granite to clay, as the latter fills the cavities. The epidote is almost colourless, with a tinge of yellow or green. Analysis gave

SiO ₂ .	FeO.	Fe ₂ O ₃ .	Al ₂ O ₃ .	CaO.	H ₂ O.	Total.	Sp. gr.
39.51	1.66	6.42	30.33	19.59	2.49	100.00	3.308

L. J. S.

Alteration of Garnet. By HEINRICH BARVÍŘ (*Zeit. Kryst. Min.*, 1895, 25, 431; from *Ber. böhm. Ges. Prag.*, 1894 (1893), No. XXVII).—In amphibolite pebbles from Hrubšitz, in Moravia, the garnets are surrounded by a zone of pale-green diopside, basic plagioclase, and fibrous hornblende, these having been produced, together with the separation of ilmenite, by the alteration of the garnet and the enclosed quartz. These alteration products are produced when garnet is fused.

L. J. S.

The Garnet Group. By ERNST WEINSCHENK (*Zeit. Kryst. Min.*, 1895, 25, 365—378).—Two sub-groups are distinguished. (1) Lime-garnets; (2) ferrous-, magnesia-, and manganous-garnets. The members of each of these groups show complete mixing amongst themselves, but there is only a slight mixing of the two groups, except sometimes in the case of lime- and manganous-garnets. The garnets which occur as primary constituents in igneous rocks are isotropic, whilst those of secondary origin in metamorphic rocks show optical anomalies; thus lime-garnets without titanium, and some manganous- and ferrous-garnets are optically anomalous, whilst titaniferous lime-garnets, most iron-garnets, and all magnesia-garnets are isotropic. The optical characters are related to the paragenesis, structure of the crystals, and the chemical composition.

L. J. S.

Baumontite from Sweden. By NILS O. HOLST (*Zeit. Kryst. Min.*, 1895, 25, 426; from *Sveriges Geol. Undersökning*, Ser. C, No. 110, 19).—Yellow crystals of baumontite, coated with hydrated iron oxide, from drusy cavities in the rhyolite-breccia, near Mien Lake, in Blekinge, gave the following results on analysis by H. Santesson. The material was dried at 100°.

SiO ₂ .	Al ₂ O ₃ .	CaO.	MgO.	K ₂ O.	Na ₂ O.	H ₂ O.	Total.
59·83	16·40	5·28	1·05	1·08	1·78	14·78	100·20

L. J. S.

Analysis of Emerald (P). By ORAZIO REBUFFAT (*Jahrb. f. Min.*, 1896, i, Ref. 27; from *Lab. chim. R. scuola app. gl'ingegneri, Napoli*, 1894, 11—14).—A substance used in jewellery as emerald gave on analysis

SiO ₂ .	Al ₂ O ₃ .	FeO.	BeO.	X'.	X''.	CaO.	MgO.	Total.
49·91	28·66	2·25	7·34	0·49	7·66	1·96	1·60	99·87

This deviates considerably from the composition of emerald, as also does the sp. gr. of 3·139; and it is doubtful whether the material is an artificial product (perhaps by melting up smaller stones), or is an unknown mineral.

L. J. S.

Amphibole [Hornblende] and Sodalite from the Trachyte of Montesanto, Naples. By P. FRANCO (*Zeit. Kryst. Min.*, 1895, 25, 328—333).—*Hornblende*: delicate, needle-shaped, brown or black crystals from cavities in the trachyte of Montesanto (*Geol. Mag.*, 1889, [3], 6, 74), show a development of the faces, which points either to hemihedrism of the monosymmetric system, or to the anorthic system, the latter with a close approach to monosymmetric angles. Analysis, on a small amount of material, gave

SiO ₂ .	Fe ₂ O ₃ .	Al ₂ O ₃ .	CaO.	MgO.	MnO.	Total.	Sp. gr.
40·79	27·40	7·01	11·54	10·60	0·90	98·24	3·06

Sodalite.—The crystals from the same trachyte are described; amongst them are groups consisting of four crystals twinned together, leaving a central hollow space. The material is colourless and transparent; isotropic, index of refraction for sodium light, 1·483; sp. gr. 2·198. Analysis gave

SiO ₂ .	Al ₂ O ₃ .	Na ₂ O.	CaO.	Cl.	Fe ₂ O ₃ .	MgO.	K ₂ O.	Total.
38·11	30·37	20·65	3·55	7·01	trace	—	—	99·69

L. J. S.

Knopite, a new Mineral near Perofskite, from Alnö, Sweden. By P. J. HOLMQUIST (*Jahrb. f. Min.*, 1895, ii, Ref. 412—416; from *Geol. För. Förh.*, 1894, 16, 73—95).—Minerals at first thought to be perofskite and dysanallyte are here described under the new name knopite, of which two types are distinguished.

Type I. This is found as lead-grey crystals of metallic lustre, about 5 mm. across, in crystalline limestone from Långarsholm, and is associated with garnet, titano-magnetite, dark green mica, and apatite; it also occurs in the serpentine-like masses enclosed in the limestone. The crystals are pseudocubic, and show dull octahedral faces, with smaller cube faces, which are bright and often conically rounded. By reflected light, a complicated lamellar structure, similar to that of perofskite, is seen. Very thin sections are translucent, and strongly doubly refracting, an eccentric optic axis being seen in

places through a cube plane. Fresh crystals have $H = 5-6$, fracture uneven, and sp. gr. 3·8902; the sp. gr. of the purified powder being 4·1101. The mineral is decomposed by a mixture of hydrofluoric and sulphuric acids. Analysis gave

SiO_2 .	TiO_2 .	ZrO_2 .	FeO .	MnO .	MgO .	Yt. earths(?).	Ce_2O_3 .
1·29	58·74	0·91	3·23	0·31	0·19	0·06	5·80
CaO .	K_2O .	Na_2O .	H_2O .	Total.			
26·84	0·75	0·29	1·00	99·41			

This reduces to RO, TiO_2 ; ZrO_2 replacing TiO_2 , whilst the silica is considered as an impurity.

Type II. This occurs in the Långarsholm limestone, and also in a breccia, from the margin of the nepheline-syenite at Norrvik, which consists mainly of serpentine-like masses with apatite, nepheline, and some calcite. The small black cubes of knopite have a metallic lustre; interpenetrating twins on (111) occur, but no lamellar structure is observed on the cube faces. Very thin splinters are translucent, doubly refracting, and pleochroic, and show traces only of lamellar structure. $H = 5-6$; fracture uneven. The mineral from Norrvik has sp. gr. = 4·21 (Anal. I); that from the limestone has sp. gr. = 4·288 (Anal. II and III).

	TiO_2 .	FeO .	Ce_2O_3 .	MgO .	CaO .	Na_2O .	K_2O .	H_2O .	Total.
I.	54·12	4·19	6·81	—	33·32	0·79	0·38	0·21	99·82
II.	56·30	5·15	4·46	0·35	32·22	0·39		0·30	99·17
III.	54·52	4·94	4·42	0·32	32·84	1·68		0·92	99·61

The slight deviation from the formula RO, TiO_2 is explained by impurities (especially water and alkalis) and by decomposition.

L. J. S.

[Hainite in the] **Phonolites of N. Bohemia.** By JOS. BLUMRICH (*Tsch. Min. Mitth.*, 1893, 13, 472—478).—In the ground-mass of the nepheline-phonolites of Hohen Hain, and other localities in N. Bohemia, are small, yellow, glassy needles and plates of a triclinic mineral, to which the name *hainite* is given. It is a silicate of sodium, calcium, titanium, zirconium, and cerium (?); sp. gr. 3·18; and is distinguished by its optical characters from the related minerals rinkite, lävenite, rosenbuschite, &c., these being the titanium and zirconium silicates, with fluorine, of elæolite-syenites. L. J. S.

Quartz-keratophyre of the Baraboo Bluffs, Wisconsin. By SAMUEL WEIDMANN (*Jahrb. f. Min.*, 1896, i, Ref. 266—267; from *Bull. Univ. Wisconsin*, 1895, 1, 35—36).—The rock is effusive, and associated with quartzite; it contains numerous porphyritic feldspars (anorthoclase and albite), quartz as strongly corroded grains, abundant biotite, and the accessories ilmenite, zircon, and magnetite. The ground-mass consists of holocrystalline quartz and feldspar; fluidal, poikilitic and sperulitic structures are shown. Two analyses gave

	SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	FeO.	CaO.	MgO.	K ₂ O.	Na ₂ O.	H ₂ O.
I.	71·24	12·20	1·71	5·44	0·98	0·13	1·86	4·29	0·81
II.	73·00	15·61	—	1·95	0·79	—	0·88	4·95	1·06
			MnO.	SO ₃ .	Total.	Sp. gr.			
I.			0·97	—	99·63	—			
II.			—	0·76	99·00	2·63		L. J. S.	

Analysis of the Victoria Spring at Oberlahnstein. By C. REMIGIUS FRESENIUS (*Jahrb. Nassau. Vereins*, 1893, *Jahrg.* 46, 1—20).—Water from the new Victoria Spring at Oberlahnstein, in Nassau, is highly charged with carbonic anhydride, and has sp. gr. = 1·003969 at 17·5°; on standing, an ochre-coloured precipitate is formed, owing to the oxidation of the ferrous carbonate. Analysis gave in 1000 parts, Na₂CO₃, 0·992043; Li₂CO₃, 0·011954; Am₂CO₃, 0·005780; Na₂SO₄, 0·815738; NaCl, 1·311632; NaBr, 0·001626; NaI, 0·000011; Na₂HPO₄, 0·000978; NaNO₃, 0·004320; Na₂B₄O₇, 0·005901; K₂SO₄, 0·051616; K₂CO₃, 0·353078; SrCO₃, 0·000359; MgCO₃, 0·255014; FeCO₃, 0·012678; MnCO₃, 0·000878; SiO₂, 0·021676 = 3·845232; CO₂ (in bicarbonates), 0·715417; CO₂ (free), 1·515098 = 6·075797. Also traces of Rb₂SO₄, Cs₂SO₄, Na₃AsO₃, aluminium compounds, and organic matter. The water is compared with other table waters.

L. J. S.

Physiological Chemistry.

Digestion of Trehalose. By EMILE E. BOURQUELOT and EUGÈNE GLEY (*Compt. rend. Soc. Biol.*, 1895, **11**, 555—557).—Maltose is converted into glucose by intestinal juice, pancreatic juice, and blood serum. Cane sugar and trehalose are similarly acted on by the intestinal juice, but resist the action of the ferment found in pancreatic juice and blood serum.
W. D. H.

Passage of Sodium Iodide from the Blood to the Lymph. By LAFAYETTE B. MENDEL (*J. Physiol.*, 1896, **19**, 227—239).—This is a contribution to the vexed question of lymph formation. The author supports Heidenhain's view that physical processes will not explain lymph formation. Sugar and sodium chloride occur in greater amount in lymph than in blood, and the same is true for sodium iodide after injection into the blood stream.

These facts are considered to bear out the doctrine of lymph-secretion.
W. D. H.

Chemical Composition of Enamel. By CHARLES S. TOMES (*J. Physiol.*, 1896, **19**, 217—223).—Great discrepancies exist in the analyses of the enamel of the teeth, various investigators giving numbers varying from 2 to 11 per cent. of organic matter. The organic

matter is generally estimated by loss, and water is never set down as a constituent. The present paper shows that the loss on ignition is due to water, and, on attempting to estimate the organic matter directly, none was found, or a quantity too small to be weighable. This is in favour of the excretion theory of enamel development.

W. D. H.

Relation of the Liver to Fats. By DIARMID NOËL PATON (*J. Physiol.*, 1896, 19, 167—216).—The liver is a gland which is not on the path of the fats absorbed from the intestine, but the fat can only enter it by the blood stream of the hepatic artery. The variation of the fat of the liver cells with food, nutrition, &c., is, however, a well-known fact, and the present paper seeks to elucidate some of the problems of metabolism in this direction.

After extraction with ether, the action of a mineral acid liberates a further amount of material soluble in ether (fatty acids), which is in part derived from soaps and in part from such compounds as nucleïns or lecith-albumins. The present research is concerned with the fatty acids extracted without acid. Any part of the organ may be taken for analysis, as the ether extract is uniformly distributed. In animals in the same condition, the percentage amount of substances soluble in ether is fairly uniform.

The results given in detail and in tabular form show that the ether extract of the liver gives a most imperfect indication of the amount of the essential (for nutritional purposes) constituents of the fats—the fatty acids; there must be other compounds besides normal fats present. In the first place, the liver fats contain a much smaller percentage of oleïc acid than the fats of other parts of the body; lower fatty acids are present in negligible amounts; the most important and constant compound other than fat in the liver extract is lecithin. The results recorded agree closely with those of Heffter (*Arch. exp. Path.*, 28, 97), and show that lecithin comprises 2·35 per cent. of the liver and 9·7 per cent. of the solids present. It is largest during starvation and smallest during a fat diet. The liver seems to possess the important power of utilising and economising the phosphorus of the body by combining it with fatty acids to form lecithin as a stage in its conversion into the nucleïn compounds of the body. When the amount of lecithin is large, the acidity of the ether extract is great; when small, the acidity more nearly approaches that of the body fats; but with lecithin in the mixture, it is practically impossible to arrive at the amount of free fatty acid in the extract. The amount of cholesterol found in the extract is smaller than that given by Kausch; it amounts to 8—11 per cent. of the extract. Rather more than half of the fatty acids are present in the form of neutral fats. About 12 per cent. in the mean of the extract is not yet accounted for; it is in part pigment. Evidence is adduced that the fat is not simply stored in the liver from the blood, but is produced there. It disappears after it accumulates, but whether it is simply thrown out or metabolised is not manifest. There is certainly no simple conversion as with glycogen, for in the liver kept at the body temperature

after an animal's death, but while the liver cells are still alive, there is no disappearance of the fat.

After storage from cat's milk in the case of kittens, no diminution occurs during inanition of 56 hours; but after 68 hours it has been got rid of in great measure. In pigeons, a four days' fast caused no alteration in the normal amount of liver fat. Excess of fat in the food is largely stored in the liver cell, from which it is gradually got rid of, but only after about 70 hours; there is no truth, however, in the statement that the amounts of fat and glycogen in any way correspond with one another. Diet rich in carbohydrates increases the liver fats, but not always in any marked degree; the fatty acids increase as the glycogen is disappearing, and are probably formed by the metabolism of glycogen. Excess of proteid food does not lead to an accumulation of fat in the liver.

W. D. H.

Transformation of Fat into Glycogen in the Silkworm during Metamorphosis. By E. COUVREUR (*Compt. rend. Soc. biol.*, 1895, **11**, 796—798).—On comparing the curves for the amount of fat and glycogen in the silkworm during its life history, they vary exactly inversely with one another. The loss of fat and corresponding gain in glycogen is most marked during the chrysalis stage.

W. D. H.

Assimilated Iron Compounds in Animal and Vegetable Cells. By A. B. MACALLUM (*Quart. J. Mic. Science*, 1896, **38**, 175—274; compare Abstr., 1895, **ii**, 518).—The paper relates to iron compounds other than hæmoglobin and hæmatin, and discusses their distribution in different parts of the animal and vegetable kingdom. The facts described indicate that a substance in which iron is firmly held is a constant constituent of the nucleus of the cytoplasm of non-nucleated cells, and in the cytoplasm of ferment-forming cells. This substance, chromatin, is not constant in its molecular structure, but its most marked character is the occurrence in it not only of iron but of nucleïn or nucleic acid. The iron is possibly united to the carbon of the nucleïn; acid alcohols liberate it as a ferric salt, but this is no proof that it occurs in the ferric state in the nucleus.

It is difficult to state any difference between animal and vegetable cells. As a rule it is easier to liberate the iron with ammonium sulphide in vegetable cells; the same reagent liberates the iron of free hæmatin, although it does not affect hæmoglobin. Hæmoglobin is derived from chromatin, but is present in no vegetables; hence, probably, the iron is combined in animal chromatin in a way unlike that in which it is held in the vegetable cell. The use of iron absorbed from the soil is obvious, and a lack of iron affects not only the formation of chlorophyll, but strikes at the very life of vegetable cells. In the same way anæmia or chlorosis in vertebrates is not a lack of hæmoglobin due to want of organic or inorganic iron compounds in the food, and directly absorbed by the intestine, it is really due to a want of chromatin in the cells; and chlorosis may in this sense occur in animals which have no hæmoglobin. Chromatin has an oxygen-holding function like that of hæmoglobin, and this is intimately

related to the life of a cell. In vegetables, the two processes of respiration and assimilation seem to involve two iron compounds in the same nucleus. The full consideration of this question, together with that of the rôle of sulphur and phosphorus in the nucleïn, is postponed.

W. D. H.

Intestinal Absorption of Peptone. By E. WAYMOUTH REID (*J. Physiol.*, 1896, **19**, 240—261).—Grübler's peptone was used as a test proteid. After precipitation by alcohol, it dissolves in hot (70°) 5 per cent. trichloroacetic acid; and all other proteids in the secretions of the gut are precipitable by the addition of an equal volume of 10 per cent. trichloroacetic acid; to the filtrate, 10 per cent. of hydrochloric acid is added, and then a saturated solution of phosphotungstic acid to complete the precipitation. Nitrogen is estimated in this precipitate by the Kjeldahl process.

To recover unabsorbed peptone from the gut, very careful washing is required, and certain precautions, described in detail, are necessary. Experiments were made on dogs, loops of the intestine being measured off, and tied by tapes; into these recently exposed loops the peptone was injected; parallel experiments were always conducted on two loops. After a quarter of an hour, the dogs were killed, the loops were removed, and their contents examined. A table of six experiments is given, showing an absorption of from 40 to 70 per cent. of the peptone introduced; the difference between the two loops was never more than 5 per cent.

W. D. H.

Urea in Animal Organs. By BERNHARD SCHÖNDORFF (*Pflüger's Archiv*, 1895, **62**, 332).—By means of the method previously described by the author (this vol., ii, 131) he finds in the organs of a dog, with the exception of the muscles, heart, and kidneys, urea in quantity corresponding with that in the blood.

The muscles contain urea. This is a direct contradiction of the work of previous physiologists; it is present in too large an amount to be accounted for by the blood in the muscles.

Urea is a constituent of the red corpuscles, and is indeed about equally divided between blood corpuscles and blood serum.

W. D. H.

Physiological Action of Want of Oxygen. By JACQUES LOEB (*Pflüger's Archiv*, 1895, **62**, 249—293).—From a number of observations and experiments on the eggs of *Ctenolabrus*, and on the heart of the embryo of the same animal, the conclusion is drawn that want of oxygen first produces molecular and then morphological changes in the cells, which are the cause of bringing the vital activity of the organism to an end. Some of the cells of this animal become liquid with the loss of oxygen, but on admission of air they are formed afresh. In embryos, like that of the *Fundulus*, deprivation of oxygen produces no change in the cells of the heart, which continues beating for many hours, whereas in *Ctenolabrus* the change in the cells is marked, and the standstill very suddenly produced.

W. D. H.

Comparison of the Action of Cadmium and Zinc Salts. By ATHANASIU and PAUL LANGLOIS (*Compt. rend. Soc. Biol.*, 1895, **II**, 496—497, 719—722).—The symptoms of poisoning by zinc and cadmium salts are identical; the dose only differs. The most marked symptom is muscular paralysis, the cerebral centres being first affected; the heart, moreover, is slowed and weakened, being governed only by its own local ganglia. The experiments were made on frogs and turtles, but in all experiments a difficulty was found in obtaining blood serum free from hæmoglobin. Experiments made on Hamburger's plan showed that the injection modified the isotony of the blood, leading to a liberation of hæmoglobin, a partial formation of hæmatin, an increase in the amount of serum-globulin, and a general profound alteration in the red corpuscles, especially with cadmium salts.

W. D. H.

Indican and Indole in the Tissues of Tumours. By NEPVEU (*Compt. rend. Soc. Biol.*, 1895, **II**, 475—476).—In five specimens of cancerous tumours, indican and indole were found.

W. D. H.

Behaviour of Caffeine and Theobromine in the Organism. By MANFREDI ALBANESE (*Gazzetta*, 1895, **25**, ii, 298—321).—The administration of large doses of caffeine to dogs is followed by a greatly increased secretion of urine, from which a monomethylxanthine, $C_6H_5N_4O_2$, probably identical with that obtained by Salomon (*Abstr.*, 1886, 266), may be separated. A dose of 1 gram of methylxanthine administered hypodermically to a dog weighing 8 kilos. caused death in 10 days; in smaller doses, it acts as a diuretic, and must be considered as an intermediate product in the transformation which caffeine undergoes in the organism, for very little of it is excreted when hypodermically injected. After the administration of caffeine in the food of a dog, small traces of it can be extracted from the urine.

Xanthine is not a normal constituent of the urine of rabbits; after administering caffeine, the urine contains small quantities of caffeine but no methylxanthine. A dimethylxanthine, $C_7H_8N_4O_2$, and caffeine can be separated from human urine after caffeine has been taken internally.

It is thus evident that in its passage through the organism, methyl groups are removed one by one from caffeine until xanthine is finally obtained, and converted into ammonia and urea.

Methylxanthine, injected into the jugular vein of rabbits, acts as a very powerful diuretic, the secretion of urine being increased to more than 40 times the normal.

Theobromine, when administered internally to dogs, behaves like caffeine; small quantities of it are excreted, and a larger proportion appears in the urine as methylxanthine.

W. J. P.

The Cholesterol of Human Fæces. By STANISLAS BONDZYŃSKI (*Ber.*, 1896, **29**, 476—478).—Human fæces contain a substance which is apparently closely connected with cholesterol, but differs from it in some important particulars; to this the author proposes to

give the name *koprosterol*. This substance can be extracted from the fæces by the application of the usual method for isolating cholesterol. It is insoluble in water and alkalis, soluble in alcohol, chloroform, ether, carbon bisulphide, benzene, and light petroleum. It crystallises in long, slender, pliable needles, melts at 95—96°, and is dextro-rotatory, $[\alpha]_D = +24^\circ$.

Analyses lead to the formula $C_{25}H_{44}O$, whilst the formula of cholesterol is $C_{27}H_{46}O$. The *benzoate* crystallises in rectangular tablets, and melts at 114—115°. *Koprosterol* gives the same colour reactions as cholesterol; it never appears to be accompanied by the latter in the fæces.

A. H.

Chemistry of Vegetable Physiology and Agriculture.

Fractional Fermentation of Cane Sugar with Pure Yeasts.

By WILLIAM L. HIEPE (*J. Fed. Inst. Brewing*, 1895, **1**, 288—322).—A considerable number of experiments are described, in which solutions of cane sugar were fermented with pure cultures of various types of yeast. Samples were withdrawn for analysis before the addition of the yeast, five minutes after the latter had been added, and afterwards at intervals of 24 hours, the fermentation being conducted at the ordinary temperature. Amongst the results recorded, it was found that the rate of inversion, and also of fermentation, varied greatly with different species of yeast. Thus, the smallest percentage of cane sugar inverted during the first five minutes was 1.95, and was produced by Chesters' yeast, whilst the greatest inversion occurring within the same period was 58.85, and was produced by a low fermentation yeast (Jørgensen's No. 84). In the case of two low fermentation yeasts (Jørgensen's Nos. 84 and 304), inversion was complete within 24 hours, whilst the longest time for complete inversion was 11 days (*Sacch. exiguus*), Chesters' yeast requiring 7 days. There appears to be no close relationship between the rates of inversion and fermentation by a yeast, although in several cases a slow inversion corresponds with a slow fermentation. In all cases, the dextrose is fermented more rapidly than the levulose, the amounts of the former fermented within 24 hours varying between 1.27 and 22.88 per cent., the corresponding numbers for levulose being 0.19 and 14.04 per cent. for the same yeasts. Towards the end of the fermentations, the quantities of the two sugars fermented approximate to one another, and the last portions disappear together. In order to determine whether there is any retarding action on the fermentation owing to the fact that the yeast has first to invert the cane sugar, experiments were made in which the cane sugar was first inverted, and then the rate of fermentation of the resulting invert sugar was determined. It was found that in the case of No. 84 yeast (which inverts rapidly) the rate of fermentation was nearly the same as with

cane sugar, whilst in the case of Chesters' yeast (which inverts slowly) there was a considerable increase in the rate of fermentation.

A. K. M.

Bacterial Infection by Air-sown Organisms. By HORACE T. BROWN and G. HARRIS MORRIS (*J. Fed. Inst. Brewing*, 1895, 1, 14—21).—In this paper the authors show how they were able to trace to its source (putrefying offal and other filth in adjoining premises) a case of bacterial infection in a certain brewery, the beers of which had from time to time shown a tendency to develop *ropiness* or viscosity. The particular organism associated with this malady was not the *Bacillus viscosus* of van Laer, but a small *coccus* occurring in the diad and tetrad form. Although the organism mentioned was invariably found in all samples of the ropy beer, the authors were able in only one or two cases to induce ropiness by its addition to sterile beer; the production of viscosity evidently depending on certain conditions of nutriment which were not present in all beers.

A. K. M.

Bacillus subtilis. By ADRIAN J. BROWN (*J. Fed. Inst. Brewing*, 1895, 1, 423—426).—The non-identity of *Bacillus subtilis* with the long, thin bacterium found in ale of doubtful stability has been established by van Laer, who named the latter *Saccharobacillus pastorianus*. Owing to the abundance of *Bacillus subtilis*, however, this organism must frequently gain access to brewers' worts and ales, and the author has therefore made some experiments, in order to ascertain if it can become a source of danger. He finds, however, that this organism cannot grow in either wort or beer having a normal acidity. If the acidity is neutralised by the addition of calcium carbonate, a growth of the organism will readily occur, although the growth in the neutralised wort is not as vigorous as in the neutralised beer. It was also found that a growth of *B. subtilis* could be obtained in a neutral infusion of hay to which 5 per cent. of dextrose was added, but when, through the action of the bacillus on the sugar, the acidity reached 0·04 per cent., the growth and action of the ferment entirely ceased. If, on the other hand, calcium carbonate was added to neutralise the acid when formed, the growth and action continued until the whole of the sugar was decomposed.

The fact that *B. subtilis* is an *aërobic* organism, and that the normal amount of acid present in wort and beer prevents its growth, shows that this organism is not a source of danger to the brewer.

A. K. M.

Alcoholic Fermentation arrested by Substances secreted by Aspergillus niger. By EMILE E. BOURQUELOT and H. HÉRISSEY (*Compt. rend. Soc. Biol.*, 1895, 11, 632—635).—Aqueous extracts of cultures of this mould contain very little solid, but act hydrolytically on cane sugar, maltose, inulin, trehalose, &c., and at the same time lessen alcoholic fermentation if yeast is added as well.

W. D. H.

Fermentation of Maltose by the Mould Eurotiosis Gayoni. By J. B. VINCENT LABORDE (*Compt. rend. Soc. Biol.*, 1895, 11, 472—474). By EMILE E. BOURQUELOT (*ibid.*, 474—475).—The first paper relates to the action of a newly discovered mould *Eurotiosis Gayoni*.

When this is added to a solution of maltose, the sugar is fermented without any appreciable formation of glucose. But the glucose is probably fermented as quickly as it is formed; and in a mixture of maltose and glucose, the latter increases for a time in quantity as the fermentation proceeds.

BOURQUELOT points out that this is always the case with moulds; maltose, like cane sugar, is not directly fermentable with yeast, but is first converted, by a soluble ferment secreted by the organism, into glucose, a statement recently confirmed by E. Fischer.

W. D. H.

Action of Friedländer's *Pneumococcus* on Sugars. By LÉON GRIMBERT (*J. Pharm.*, 1895, [6], 2, 529—533).—The author worked with *Pneumococcus* emanating from the Pasteur Institute, and having all the characters attributed to Friedländer's *Pneumococcus*, using for medium a solution containing 3 parts of fermentable sugar, 2 parts of dry peptone, and 100 parts of water, to which pure calcium carbonate was added, the whole sterilised, and, after seeding, maintained at a constant temperature of 36°. The results obtained are set forth in the following table, the weights being per cent. of the sugar used.

	Days fermenting.	Ethylie alcohol.	Acetic acid.	Lactic acid.	Succinic acid.
Glucose	30	trace	11·06	58·46	none
Galactose	10	7·66	16·60	53·33	„
Arabinose	69	none	36·13	49·93	„
Mannitol.....	38	11·40	10·60	36·63	„
Glycerol	30	16·66	19·70	45·53	„
Saccharose	60	trace	29·53	+	+
Lactose	24	16·66	30·66	trace	26·76
Maltose	68	trace	35·53	+	+
Dextrin	12	mixed with higher alcohols	10·13	none	13·96
Dulcitol	5	29·33	9·46	„	21·63
Potato	68	none	+	„	+

The sign + indicates that both acids were present, but could not be determined; no formic acid was observed in any case. It is interesting to note that mannitol gives lactic acid, whilst its isomeride dulcitol yields succinic acid, that the C_{12} sugars give both lactic and succinic acids, &c., &c. Attention is drawn to the fact that these results differ considerably, both in the character of the products and the activity of the organism, from those obtained by Frankland, Stanley, and Frew (*Trans.*, 1891, 59, 253—270), which, it is suggested, points to there being at least two forms of *Pneumococcus* (Friedländer) morphologically similar, but differing considerably in their fermentative actions; a cultivation in glycerol with chalk will determine which of the two any future worker may be dealing with.

D. A. L.

Nature of Fermentative Changes in Natural and Polluted Waters, and in Artificial Solutions, as indicated by the Composition of the Gases in Solution. By WALTER E. ADENEY

(*Trans. Royal Dublin Society*, New Series, 5, Part XI).—The author has described in this communication a method, and special apparatus, for studying, quantitatively, the changes in composition of the dissolved gases in liquids, which may accompany fermentative changes in the same.

Experimental results are given in the paper to show that for this purpose water solutions can be preserved completely out of contact with air for long periods, extending to as much as a year, without suffering appreciable loss of or gain to the gases they hold in solution, either by escape of gas, or by access of air, by simply keeping them in bottles completely filled and carefully stoppered with glass stoppers, the bottles themselves being kept immersed neck downwards, in distilled water in large glass vessels which are covered with glass plates.

The method of experiment has been modified, according as it had been desired to observe the total changes in composition of the dissolved gases during a complete, or a partial, aërobic fermentation, or to study the changes which occur progressively during an aërobic fermentation from commencement to completion, at intermediate stages.

To effect the first purpose, a strong solution of a polluted water, or of organic and inorganic substances, of known strength and composition, in either of which the quantities of fermentable matters might be regarded as in decided excess relatively to that of the dissolved oxygen therein, has been taken as the basis of a number of gradually increasing dilutions with good tap-water, or when necessary, with pure water. In this way, a series of dilutions, gradually decreasing in strength, of the solution under experiment has been obtained, and the changes in composition of the dissolved gases during fermentation, have been determined in each.

The results which have followed indicate, quantitatively, the changes which have occurred during the fermentation of the substances therein, under the varying conditions, from those in which the fermentable matters were in excess, to that in which the dissolved oxygen was in excess.

To effect the second purpose, a large quantity of a strong solution of a polluted water, or of an artificial solution of known strength and composition, and occasionally one or two dilutions thereof, have been employed. These have been allowed to ferment for a sufficient period, and the accompanying changes in composition of the dissolved gases have been determined. The portion of the solution remaining from this operation has been again aërated, and allowed to ferment for a further period, and the products of the fermentation again estimated. These operations have been repeated until the fermentation has reached a desired stage, or has been completed. In this way, it has been possible to examine the products of fermentation, as it has gradually proceeded step by step, from commencement to completion, under well defined conditions.

By the method thus briefly outlined, it has been possible to study fermentations carried on under continued aërobic conditions in all parts throughout the mass of the fermenting liquid, from commencement to completion, or to any desired intermediate stage.

In all the experiments recorded in this paper the changes in composition of the inorganic nitrogenous substances present in the solution employed, which have occurred during fermentation, have been determined in addition to the changes in composition of the dissolved gases.

The following conclusions have been drawn by the author from the experiments recorded in this paper.

1. That the method and apparatus described in the paper for preserving natural waters, or artificial solutions, out of contact with air, and for analysing the gases in solution in them before and after keeping, are capable of yielding very accurate results, and that the method is not attended with any great experimental difficulties.

2. That observations of the changes in composition of the gases in solution, which take place during the course of fermentation in the presence of mixed organisms, under the conditions described, when made in conjunction with an examination of the changes which simultaneously occur in the organic and inorganic nitrogenous substances in the water, are productive of extremely important results, and are necessary if it be desired to investigate completely the chemical changes which accompany such fermentations.

3. That with the aid of such observations it is possible to study the various chemical changes which take place progressively during the fermentation, within certain well defined conditions, of any fermentable substance or substances, from commencement to completion at any intermediate step desired.

4. That it hence becomes possible to demonstrate that the fermentation of substances under aërobic conditions, and in the presence of the organisms usually present in water, takes place progressively in two distinct stages : (1) that in which the organic substances are completely broken down, the carbon and nitrogen being largely converted into carbonic anhydride and ammonia, a little organic matter remaining as such, but in an altered form ; and (2) that in which ammonia is oxidised to nitrous or nitric acids, or both.

5. That the first stage of fermentation must be complete before the second stage can set in.

6. That the *organic* substances which result as products of the first stage of fermentation, may undergo further change during the subsequent stage, and give rise to the formation of carbonic anhydride and possibly also to nitric acid.

7. That peaty matters when present alone in a water undergo very slow change, but when present with ammonium compounds in a water, they readily undergo fermentation together with the ammonium compounds, just as the organic matters, which, as above stated, are formed during the first stage of fermentation of animal, vegetable, or artificial organic substances, do during the after-fermentation of ammonium compounds which may have been also formed thereby, or which may have been previously present or added.

8. That the above-mentioned fermented organic matters, and also peaty matters, appear to determine the *nitric* fermentation of *ammonia*, since in their complete absence, similar organisms being present, only nitrous acid is obtained.

9. That during the intermediate stages of a fermentation of mixed peaty matters and ammonium compounds, various interchanges between the two appear to take place, the character and extent of which apparently depend on the relative quantities of peaty matters, ammonia, and dissolved oxygen present, and also on the character of the peaty matters themselves, whether they have been freshly formed, or have undergone any previous fermentative changes.

10. That in the presence of small quantities of peaty, or other fermented organic matters, carbonic anhydride and ammonia may become "fixed" during fermentation, in appreciable quantities, no doubt, from Winogradsky's researches, to form organic matter.

11. That the formation of 1 part by weight of nitrous nitrogen during the fermentation of ammonia, in the complete absence of organic matter, is attended by the consumption of about 4.2 parts by weight of oxygen.

12. That for similar volumes of oxygen consumed, the quantity of nitrogen oxidised during the fermentation of ammonia is distinctly greater, in the presence of peaty or other fermented organic matters, than in their absence.

13. That for similar volumes of atmospheric oxygen consumed, the quantities of carbonic anhydride and of ammonia "fixed" are also more appreciable in the presence of those organic matters, than in their absence.

14. That the observed facts in reference to nitrification may be summarised as follows.

(a.) The nitrous organisms of soil thrive in inorganic solutions containing ammonia.

(b.) The nitric organisms of soil are gradually killed, or lose their vitality, in organic solutions containing ammonia.

(c.) The nitric organisms of soil thrive in inorganic solutions containing nitrites.

(d.) The nitrous organisms cannot oxidise nitrites to nitrates in inorganic solutions.

(e.) The presence of peaty or humus matters appears to preserve the vitality of nitric organisms during the fermentation of ammonia, and establishes conditions whereby it is possible for the nitric organisms to thrive simultaneously in the same solution with the nitrous organisms.

Query—Is it possible for either the nitrous, or nitric, or other organisms to separately set up the complete oxidation of ammonia to nitric acid, in the presence of peaty or humus matters?

15. That by determining the changes in the composition of the dissolved gases, and in that of the organic and inorganic nitrogen compounds, which accompany fermentation in natural and polluted waters, it is possible not only to differentiate easily fermentable from difficultly fermentable substances present in them, but to approximately estimate their quantity.

16. That such determinations are of very great value in the case of polluted waters, because, in addition to affording very accurate estimations of the total quantities of fermentable matters in them, in

terms of the exact volume of atmospheric oxygen necessary for their complete fermentation, it is possible by proper examination to determine what fraction of such volume is required for the first stage of fermentation, and what fraction for the second—distinctions of the utmost importance in considering the technical aspect of the question of the pollution of rivers.

A number of experiments on the fermentation of pure urea, *unmixed with any other fermentable organic substance of any kind*, are also quoted, the results of which show that the fermentation of this substance is apparently anomalous. Thus, from the earliest stage of fermentation of a very strong solution of pure urea, *aërobic conditions being established throughout the mass of the solution*, nitrous acid, in addition to ammonia, was formed, the proportion of nitrous to ammoniacal nitrogen being as 1 : 4. The author believes, however, that the chemical changes which result in this case in the formation of nitrous acid are not analogous to those attending the formation of that substance during the fermentation of ammonia, but rather to those attending the formation of fermented organic matters during the first stage of their fermentation, the nitrogen in the case of urea taking the place of the carbon in a more highly carbonated organic compound.

The author points out that a new term is required to designate the process of the first stage fermentation, described in the paper, which organic substances undergo, and proposes to employ the term "bacteriolysis" for the purpose, and to reserve that of nitrification to describe the fermentation of ammonium compounds. W. E. A.

Effect of Alkaloids on the Germination of Seeds. By UGOLINO MOSSO (*Ann. Agr.*, 1895, **21**, 544; from *Arch. ital. Biol.*, **21**, 231).—In experiments with the seeds of *Phaseolus multiflorus* it was found that cocaine and atropine* (0·01 per cent.), strychnine (0·05 per cent.), morphine (0·001 per cent.), and atropine* (0·0005 per cent.) assist, whilst more concentrated solutions retard, germination. Caffeine (salicylate) was not favourable owing, perhaps, to the presence of salicylic acid. According to the amount given, it seems that alkaloids exercise a narcotic or a stimulating effect on plants as well as on animals.

N. H. J. M.

Philothion and Laccase in Germinating Seeds. By JOSEPH DE REY-PAILHADE (*Compt. rend.*, 1895, **121**, 1162—1164).—Some germinating seeds, such as beans, peas, chick-peas, white lupins, haricots, soja, wheat, maize, chestnut, Indian chestnut, maple, and ginkgo, contain both philothion and laccase; others, such as pine kernels, contain philothion and no laccase, whilst a third group, including castor-oil seeds, radish, gourd, Marvel of Peru, bind-weed, and potato tubers contain laccase, but not philothion, and a fourth group (acorn, laurel) contains neither, or only minute traces, of these compounds.

When the seeds contain laccase, this substance is present before absorption of water has taken place; but the quantity increases continuously as germination progresses. Philothion, on the other hand,

* One of these should probably be nicotine, which was also one of the compounds experimented with.

is found in very small quantity in the dry seeds, and is concentrated in the embryo; it becomes more abundant after the seeds have been moistened, but disappears after a few days.

Under the combined action of laccase and oxygen, philothion oxidises rapidly, with production of carbonic anhydride; but laccase alone has no action on it, and in presence of oxygen alone, it oxidises very slowly. It follows that, under the influence of laccase, philothion combines rapidly with free oxygen, and produces carbonic anhydride, thus contributing to the respiration of the seeds.

C. H. B.

Distribution of Boric acid in Nature. By HENRY JAY (*Compt. rend.*, 1895, 121, 896—899).—The author has applied the method previously described (this vol., ii, 76) to the detection and estimation of boric acid in various products of vegetable origin. Wines contain from 0.009 gram to 0.033 gram per litre, the mean being 0.017 to 0.023 per litre. The ash of wine contains from 4.7 to 16.5 grams per kilo., the average being from 8 to 12 grams. The ash of the marc contains from 1.4 to 3.5 grams per kilo., the average being 2.4 to 2.7 grams. The quantity in the ash of vine leaves is only about 0.7 gram per kilo.

Examination of a large number of fruits, leaves, &c., leads to the result that the ashes of fruits, whether fleshy or stony, contain from 1.5 to 6.4 grams of boric acid per kilo.; in the ash of seaweeds, plantain leaves, chrysanthemum flowers, and onions, the quantity varies from 2.1 to 4.6 grams per kilo. *Gramineæ* and certain fungi, on the other hand, absorb very little boric acid from the soil, and their ashes contain not more than 0.5 gram per kilo. The acid can also be recognised in the ashes of many coals, and many specimens of sea salt, and also in minute quantities in some river and spring waters.

The milk and the blood of the cow, mare, and sheep contain no recognisable quantity of boric acid even in the ash from 1 kilo., but the urine of a cow contained 0.0086 gram per litre, and the urine of a horse 0.0075 gram per litre. It seems, therefore, that when boric acid is introduced in small quantities into the stomachs of animals, it is not assimilated, but is eliminated with the urine and the other excretions.

C. H. B.

Hydrogen Cyanide in *Pangium Edule* Reinlw. By M. TREUB (*Rec. Trav. Chim.*, 1895, 14, 276—280).—The author shows that the hydrogen cyanide in *Pangium edule* is not one of the substances which afterwards go to form the proteid matter.

The formation of this hydrogen cyanide does not appear to be directly affected by light, but there is apparently a definite relationship between its formation and the assimilation of carbon. In this connection, the author states that the presence of carbohydrates, and also of certain inorganic substances taken from the soil, is an indispensable condition for the formation of the acid in question. As regards the carbohydrates in the leaves of the plant, the author proves the presence of a reducing sugar, which yields phenylglucosazone, and which is, therefore, probably glucose or fructose.

In conclusion, the author considers that hydrogen cyanide is not

merely the first recognisable nitrogenous organic substance, but is absolutely the first nitrogenous organic compound to be formed, and that by its means amides, which play so important a part in vegetable physiology, may readily be formed. In support of this view, it is shown that hydrogen cyanide occurs in numerous families of plants not at all related to *Pangium*.
J. J. S.

Methylic Salicylate and Salicylic acid in the Root of Polygala of Virginia. By AUGUST SCHNEEGANS (*J. Pharm.*, 1895, [6], 2, 452—453).—Polygala root is found to contain 0.01 per cent. of methylic salicylate and 0.06 per cent. of free salicylic acid; the latter is readily detected by twice extracting 5 or 10 grams of the dried roots with ether, filtering; evaporating, treating the residue with water, and testing with ferric chloride.
D. A. L.

Accumulation of Sugar in the Root of the Beet. By LÉON MAQUENNE (*Compt. rend.*, 1895, 121, 834—837).—No explanation has hitherto been advanced of the fact that the carbohydrates elaborated by the chlorophyllous cellules travel by diffusion into the root, but do not subsequently travel back to the leaves by a similar process. It is known, however, that the carbohydrates take the form of reducing sugars when they ascend in the plant, and of saccharose when they descend. The author regards the phenomenon as one conditioned by osmotic equilibrium; if two cellules are in communication with one another, and one contains reducing sugars, and the other saccharose, then, in accordance with well-known laws, they will exchange contents. If, however, the two cellules are those of a living beetroot, since the carbohydrates can only exist in one in the form of reducing sugars, and in the other in the form of saccharose, equilibrium will never be established, although the circulation of water will continue. Since osmotic pressures are inversely as the molecular weights, it is essential to equilibrium that the concentration of the saccharose solution be double that of the reducing sugars; if, therefore, by reason of assimilation, the osmotic pressure in the leaves increases, the principles elaborated will travel towards the root, and take the form of saccharose; if the pressure in the leaves diminishes, the saccharose in the root will split up and travel into the leaves. Cryometric measurements show that the osmotic pressures of the juice of the leaves and the juice of the root are practically identical, although that of the leaves is generally slightly lower than the other, the difference being of the same order as that which usually exists between the soil and the atmosphere.

The author states, as a general principle of vegetable physiology, the law that any proximate principle can accumulate if its formation results in a reduction of osmotic pressure. For this reason, the principles that do accumulate are always of a highly condensed character.

C. H. B.

Toxicity of Copper Salts. By W. O. ALEXANDER TSCHIRCH (*Ann. Agron.*, 1895, 21, 544; from *Chem. Zeit.*, 1894, 18, No. 102).—Contrary to what is usually supposed, copper is not poisonous to plants. Whilst the sulphate, nitrate, and chloride are corrosive, plants

take up copper without injury from soils containing insoluble copper compounds. Haricots grew better in nutritive solutions to which 0.06 per cent. of copper oxide was added, than in absence of copper.

Frank and Krueger (*Ann. Agron.*, 1895, **21**, 42) showed that the copper-lime preparation had a beneficial effect on the development of potatoes.

N. H. J. M.

Transformations which Nitrogen undergoes in the Soil. By A. PAGNOUL (*Ann. Agron.*, 1895, **21**, 497—501). **Effect of Carbon Bisulphide and of Horse Dung on Denitrification.** By PIERRE P. DEHÉRAIN (*ibid.*, 501—508).—Six pots of soil (25 kilos. each) containing superphosphate (20 grams) and potassium chloride (20 grams) were further manured as follows: A, sodium nitrate (30 grams); B, the same as A with the addition of horse dung (500 grams); C same as B with the addition of carbon bisulphide (50 c.c.). The soil of these pots was kept bare from 24th May to 21st June, when grass was sown; the grass was cut 23rd July and 23rd August. A similar set of pots *a*, *b*, and *c*, where sown with white mustard. The following amounts of grass (A, B, C) and of white mustard (*a*, *b*, *c*) were obtained (in grams).

A.	B.	C.	<i>a</i> .	<i>b</i> .	<i>c</i> .
184	251	207	234	357	283

There was no denitrification under the influence of the organic manure, as was indicated by Wagner's recent experiments (*J. Agric. prat.*, 25th August, 1895). Two other sets of experiments were made similar to the above, except that ammonium sulphate (25 grams) was substituted for nitrate. The total amount of grass (D, E, F) and of mustard (*d*, *e*, *f*) were:—

D.	E.	F.	<i>d</i> .	<i>e</i> .	<i>f</i> .
182	190	179	69	229	147

The following table shows the amount of nitrogen (milligrams per cent. in soil) as ammonia, as nitrites, and as nitrates at different dates in the fallow and grass experiments (D, E, and F). The results with mustard (*d*, *e*, *f*) are also given in the paper.

Dates.	D. Am_2SO_4 alone.			E. Am_2SO_4 + dung.			F. Am_2SO_4 + dung + CS_2 .		
	N. in soil as			N. in soil as			N. in soil as		
	HNO_3 .	HNO_2 .	NH_3 .	HNO_3 .	HNO_2 .	NH_3 .	HNO_3 .	HNO_2 .	NH_3 .
24th May.	2.77	1.26	39.37	4.16	1.15	33.00	trace	0.04	50.40
11th June.	14.95	13.00	2.47	15.41	10.05	2.55	„	0.08	36.85
21st June.	18.76	23.11	1.54	22.08	15.52	0.69	„	0.84	28.14
8th July..	11.89	0.12	0.63	13.79	0.14	0.63	15.53	6.75	0.67

In these experiments, there is again no evidence of denitrification under the influence of the organic manure. In experiment F (with carbon bisulphide), nitrification was suspended for a considerable time. In comparing the results obtained with nitrate and with ammonium sulphate respectively, it is seen that nitrate was the more efficacious, both with grass and with mustard.

As regards the effect of carbon bisulphide in checking nitrification, Dehérain calls attention to Girard's experiments (*Ann. Agron.*, 1894, 20, 478) with beet, and points out that great loss of nitrogen (through drainage) may be prevented or diminished by hindering nitrification in this manner; the following year nitrification would be energetic and produce large crops. The different results obtained by Pagnoul and by Wagner respecting the denitrifying effect of horse dung may possibly be due to the horses having been differently fed, and on the consequent difference in the nature of the micro-organisms present in the fæces. Thus, according to Bréal (*Ann. Agron.*, 18, 181) leguminous plants reduce nitrites less vigorously than gramineous plants, so that the fæces of a horse fed with oats and lucerne hay with a little straw would reduce nitrates more readily than if gramineous hay and much straw had been given in addition to oats.

N. H. J. M.

Action of Sodium Chloride and Nitrate and of Phosphates on the Solubility of the Potassium of the Soil. By NAPOLÉONE PASSERINI (*Ann. Agron.*, 1895, 21, 494; from *Atti. R. Accad.*, 1894, 75, 15).—Soil, in quantities of 500 grams, to which sodium chloride, mono- and tri-calcium phosphates, and sodium nitrate, respectively, (20 grams each) had been added, was kept in glass pots for six months, one set being kept damp, another dry. The soil contained $K_2O = 1.23$ per cent. At the end of the experiment, each pot of soil was extracted with 1 litre of boiling water. The moist soil treated with sodium chloride yielded 0.183 gram of soluble potash more than soil without the addition of salt, whilst in the case of the dry soil (with NaCl) there was an excess of 0.072 gram of soluble potash. Sodium chloride also caused greater solubility of lime and magnesia.

Monocalcium phosphate rendered soluble 0.0125 gram of potash in the damp soil, and 0.010 gram in the dry. Tricalcium phosphate had no appreciable effect. The effect of sodium nitrate was to give an excess of potash = 0.143 gram in the damp, and 0.097 gram in the dry soil, and to very much increase the solubility of the lime and magnesia in the soil.

It is generally useless to manure, with potash, soils which receive sodium nitrate and superphosphate.

N. H. J. M.

Analysis of the Soil by Plants. By G. LECHARTIER (*Compt. rend.*, 1895, 121, 866—870).—Although the quantities of various inorganic compounds absorbed by plants from the soil depend on the nature of the plant and the composition of the soil, the proportion of each substance so absorbed must not fall below a certain minimum amount necessary to the normal growth of the particular plant. The author's previous researches on the Jerusalem artichoke have shown that a comparison between the composition of normal leaves and that

of leaves which have changed prematurely, gives definite and valuable information as to the constituent that is wanting in the soil in an assimilable form. Some new experiments with lucerne lead to the same conclusion. A crop was grown for several years in succession on a field, parts only of which received potash manures at two different times, and it was found that as the potassium in the soil was used up, the lucerne became much thinner, the separate plants much lower in height, and the leaves smaller, yellowish, and in part discoloured.

So far as the proximate composition of the organic portion of the plant is concerned, the different crops showed no practical differences. The inorganic constituents of the plants with normal development, varied between the limits already known, and the composition of the separate plants on each plot was remarkably constant. Further, the plants which changed prematurely did not differ appreciably from the normal plants in the proportions of calcium, magnesium, phosphoric acid, or sulphuric acid which they contained, but the proportion of potassium in the atrophied plants was only half that in the normal plants, and was in fact reduced from 1.567 per cent. of potassium oxide in the dried plant to 0.742 per cent. This last quantity may be regarded as a minimum proportion below which the lucerne ceases to grow in a normal manner.

C. H. B.

Field Experiments [with Wheat and Barley] at Grignon in 1895. By PIERRE P. DEHÉRAIN (*Ann. Agron.*, 1895, 21, 545—565; compare *Abstr.*, 1895, ii, 179.)—In the north, where farmyard manure and commercial manures are largely employed, the rotation is generally reduced to two courses, wheat and beet, with lucerne occasionally; in some parts where beet is replaced by mangel-wurzel or potatoes, and barley and clover are included in the rotation, it is found advisable to grow wheat after roots (manured), or else, as in the Norfolk rotation, in the fourth course after the leguminous crop. Both after well manured roots and after Leguminosæ, very good crops of wheat are obtained, but it may be advisable to apply a little sodium nitrate, and perhaps also superphosphate in the spring; and attention is again drawn to the great benefit derived by careful preparation of the soil, by which nitrification is much increased.

The field experiments now described are a continuation of the earlier ones; different varieties of wheat were employed and the manuring and treatment of the soil were varied. The results are given in full in tables.

Australian wheat, without direct manure, yielded 40 metric quintals of grain per hectare, both after beet and after potatoes, whilst two other varieties (Scholley and Porion) gave much smaller yields, even when they received sodium nitrate in small quantity. When Australian wheat succeeded a leguminous crop, the yield was only an average one, even with direct manuring in addition to the residue left by the leguminous plant.

The application of nitrate had a remarkably slight effect on the crops, and this is supposed to be due to the active nitrification rendering such application superfluous. The temperature from October to December had been relatively high.

N. H. J. M.

Employment of Quicklime in the Cultivation of Leguminosæ. By AUGUST SALFELD (*Ann. Agron.*, 1895, 21, 535—536; from *deut.-landw. Presse*, 1894, 21, 785).—A poor sandy soil, for a long time cultivated, and well manured with kainite and basic slag in 1893, was divided into two halves, to one of which quicklime (2000 kilos. per hectare) was applied in the summer, to the other marl (containing a corresponding amount of lime). The following February (1894) some plots were inoculated with soil from old pea land, and were subsequently sown with peas (two kinds). Two kinds of lentils and *Lathyrus clymenum* were also sown, but for these, the soil was not inoculated. In June, after frequent rain, the marled plots were well covered with green vegetation, whilst the plants of the limed plots were generally yellow. Nodules were found on the roots of the green plants, but not on those of the yellow plants.

The following amounts in kilograms per hectare were obtained.

	<i>Pisum sativum</i> (inoculated).	<i>Pisum arvense</i> . (inoculated).	Lentils (not inoculated).
Marl.	2459	2613	894
Quicklime	804	1368	173

The quicklime destroyed the nodule bacteria and should not be applied to soil on which it is intended to grow *Leguminosæ*, but if marl is not available, the soil may be limed for cereals which precede *Leguminosæ*; in this case it might be necessary to inoculate the soil.

N. H. J. M.

Analytical Chemistry.

Gas Analysis. By M. SCHATERNIKOFF and IWAN M. SETSCHENOFF (*Zeit. physikal. Chem.*, 1896, **18**, 563—571).—The authors describe a modification of Bunsen's apparatus for eudiometric gas analysis, which is capable of speedier and more accurate measurements than the ordinary form. Illustrations of the apparatus are given, and the methods of the analysis described, whilst examples of the analysis of air show that the apparatus is capable of yielding consistent and accurate results. L. M. J.

Characteristic Colour Reaction for Chlorates. By GEORGES DENIGÈS (*J. Pharm.*, 1895, [6], **2**, 400—402).—One or two drops of the suspected liquid is mixed with 2 c.c. of pure sulphuric acid, and cooled by immersion and agitation in cold water; 5 drops of the resorcinol solution already described (this vol., ii, 337) is added steadily, the tube again immersed in cold water, and gently shaken; if the amount of chlorates in the solution does not exceed 2 per cent., a green coloration is produced, even with 0.00001 gram of a chlorate, so the test is best made in a dilute solution, 0.2 per cent., for instance. Nitrates, under similar conditions, give a feeble, yellow coloration,

changing to violet-red on heating. The strong coloration due to a nitrite would mask the chlorate colour, so nitrites must be removed by treating 2 or 3 c.c. of the solution with 1 or 1.5 c.c. of ammonia, filtering, supersaturating with acetic acid; evaporating 1 or 2 c.c. to 4 or 5 drops by boiling in a tube and shaking, then adding 10 to 15 drops of water, and treating the solution as above with sulphuric acid and resorcinol solution. Chromates, permanganates, &c., are removed by means of ammonium sulphide, and the solution subsequently supersaturated with acetic acid, &c., before testing for chlorates. Iodides should also be eliminated. Nitrates may be tested for by sulphuric acid and ferrous sulphate in the solution after the removal of the nitrites with ammonia and acetic acid. Thus the sulphuric acid solution of resorcinol, along with ferrous sulphate, permits of the detection of tartrates, nitrites, nitrates, and chlorates in the same solution.

D. A. L.

Estimation of Oxygen in Commercial Copper. By BERTRAM BLOUNT (*Analyst*, 21, 57—61).—The oxygen in metallic copper is generally assumed to be in the state of dissolved cuprous oxide, but a considerable fraction may be present in other forms, such as lead oxide, lead arsenate, &c.

After many trials, the author thinks that the best process for estimating this impurity is to fuse the sample in a current of pure hydrogen and weigh the water produced. The hydrogen is evolved from zinc and sulphuric acid, and, after passing through a wash-bottle containing solution of copper sulphate, it is freed from moisture by means of a sulphuric acid drying tube. To remove traces of oxygen, the gas is then passed through a bulb-tube of platinised asbestos, gently heated, and any moisture is then again absorbed in a second sulphuric acid tube (calcium chloride should not be used). The gas then enters a porcelain tube, inside which is placed a porcelain boat containing 10 to 15 grams of the sample, which is gradually heated by means of a small injector furnace until the metal is perfectly melted.

The water formed in this operation is absorbed in a weighed sulphuric acid tube, protected by a sulphuric acid guard-tube. After the hydrogen has passed for another five minutes, the tube is disconnected, the hydrogen is displaced by a current of dry air, and the tube is reweighed.

L. DE K.

Influence of Sulphurous Anhydride in Coal Gas Flames on Quantitative Estimations. By EDUARD MULDER (*Rec. Trav. Chim.*, 1895, 14, 307—316).—The author has made experiments to determine what effect, if any, the sulphurous anhydride of coal-gas flames has on various estimations. He comes to the conclusion that the estimation of barium as barium carbonate is not affected to any appreciable extent in working at fairly high temperatures with a platinum crucible which is kept covered. In the actual experiments, the calcined residue, when treated with hydrochloric acid, gave traces of barium sulphate, but these were too small to determine accurately.

By supporting the crucible in a hole made in an asbestos plate, the author finds that he can heat the crucible at a fairly high temperature without a lid, and that no sulphurous anhydride will be absorbed. A porcelain crucible may also be substituted for the platinum one. At extremely high temperatures, the platinum becomes porous to sulphurous anhydride, and a small quantity of the barium carbonate is decomposed into the oxide and carbonic anhydride, the former attacking the platinum.

In many estimations, better results are obtained by heating at a moderate temperature for a long time, rather than at a high temperature for a short time.

J. J. S.

Estimation of Selenious and Selenic acids. By FRANK A. GOOCH and A. W. PEIRCE (*Zeit. anorg. Chem.*, 1896, **11**, 249—253; *Amer. J. Sci.*, [4], **1**, 31—34).—In the estimation of selenious acid by distilling it with potassium iodide and an acid, according to the method previously described by Gooch and Reynolds (this vol., ii, 124), a small quantity of iodine always remains in the distillation flask, and this necessitates two titrations of the iodine. To avoid this double titration, the authors proceed as follows. The selenious acid is mixed with a measured quantity of a concentrated solution of potassium iodide which has been standardised against arsenic acid, a solution of acid potassium arsenate and dilute sulphuric acid is then added, and the mixture distilled, as previously described. The residue in the distillation flask is neutralised with potassium hydroxide, and an excess of a concentrated solution of potassium hydrogen carbonate added. It is then titrated with normal iodine solution. This gives the quantity of iodine equivalent to the arsenious acid, that is, the amount of iodine liberated by the arsenic acid; the difference between this and the amount of iodine originally present as potassium iodide gives the amount of iodine liberated by the selenious acid. The results obtained are accurate.

When selenic acid is to be estimated, it is first reduced to selenious acid by boiling with potassium bromide and sulphuric acid, and then the selenious acid is estimated, as described above.

E. C. R.

Estimation of Phosphoric acid in Soils by Precipitation with Molybdic Solution, and Titration of the Ammonium Phosphomolybdate. By C. B. WILLIAMS (*J. Amer. Chem. Soc.*, 1895, **17**, 925—926).—The author recommends the following process, the hydrochloric acid extract of the soil is obtained by digesting the sample in acid of 1.115 sp. gr. at 100° for 10 hours, the organic acid (1 per cent. citric acid and 0.63 per cent. oxalic acid solution) extracts being obtained by digesting at ordinary temperature for five hours. To destroy all organic matter in the first extract, an aliquot part is mixed with one-third of its volume of nitric acid and evaporated until only 2—3 c.c. is left; in the second case, the liquid is evaporated to dryness and ignited with the addition of nitric acid until the organic matter is completely destroyed.

The residues are now dissolved and made up to convenient volumes, and portions corresponding with 2—20 grams of soil (according to

the supposed richness in phosphoric acid) are first mixed with 15 grams of ammonium nitrate, and, after heating to 40°, precipitated with 30 c.c. of the conventional molybdate solution. After four hours, the precipitate is collected and twice washed with water; it is now dissolved in dilute ammonia, and nitric acid is added until the precipitate begins to re-form; 10 grams of ammonium nitrate is added, also 2 c.c. of nitric acid, and, after five minutes, 2 c.c. of molybdate solution. The now very pure molybdate precipitate is collected and titrated according to the author's process.

L. DE K.

Estimation of Phosphoric acid by the Molybdate-Magnesia Method, and by a Volumetric Method. By B. W. KILGORE (*J. Amer. Chem. Soc.*, 1895, 17, 941—943).—The author has again submitted solutions of disodium hydrogen phosphate of known strength to a number of analysts, with the request to estimate the phosphoric by the molybdate-magnesia method and by the (American) volumetric process.

On the whole, the volumetric estimations were the best, the gravimetric ones being in many instances considerably in excess of the truth.

L. DE K.

Estimation of Phosphoric acid by Titration of the Ammonium Phosphomolybdate Precipitate with Standard Alkali. By B. W. KILGORE (*J. Amer. Chem. Soc.*, 1895, 17, 950—968).—If the sample contains much organic matter, 2 grams is ignited with magnesium nitrate, and then dissolved in hydrochloric acid. Ordinary phosphates and fertilisers are dissolved in 30 c.c. of strong nitric acid containing a little hydrochloric acid, or in 30 c.c. of warm hydrochloric acid with gradual addition of 0.5 gram of potassium chlorate. Phosphates rich in iron or aluminium are dissolved in 15—30 c.c. of hydrochloric acid, and 5—10 c.c. of nitric acid. The solution is made up to, say, 200 c.c., and a suitable portion is taken for analysis.

After adding about 5 or 10 c.c. of nitric acid, ammonia is added, until a precipitate just begins to form, and the liquid is diluted to 60 or 100 c.c., and then, after heating to 65°, precipitated with a slight excess of filtered molybdate solution (100 grams of molybdic acid, 400 grams of ammonia, sp.gr. 0.96, 1500 grams of nitric acid, sp. gr. 1.2, and 80 c.c. of nitric acid, sp. gr. 1.42). After six minutes, or, if the sample is very poor, eight or ten minutes, the liquid is filtered as quickly as possible through a 3-in. Hirsch funnel, the perforations of which are covered with a disc of soft filter-paper, or in a Gooch crucible, with one or two pieces of filter-paper slightly larger than the bottom of the crucible, using the filter pump in both cases. The precipitate is twice washed by decantation, using 50—75 c.c. of dilute nitric acid (1—10, of 1.42 sp. gr.), then once with the same amount of 3 per cent. solution of ammonium nitrate, and finally washed on the filter, until the washings are no longer acid; this generally requires 250 c.c. of water.

The precipitate is now rinsed back into the beaker and dissolved in a known amount of standard potash, the excess of which is titrated back with standard nitric acid, using phenolphthaleïn as indicator.

If the alkali contains exactly 18·17106 grams of potassium hydroxide per litre, 1 c.c. equals 0·001 gram of P_2O_5 . L. DE K.

Gravimetric Method of Estimating Phosphoric acid as Ammonium Phosphomolybdate. By THOMAS S. GLADDING (*J. Amer. Chem. Soc.*, 1896, **18**, 23—27).—The direct weighing of the yellow precipitate has often been attempted, with but indifferent success. The author has succeeded in obtaining a precipitate which, after drying at 105° , contains exactly 3·76 per cent. of phosphoric anhydride.

The solution of the phosphate is mixed with an equal bulk of strong ammonia, and strong nitric acid is then added to acidity. The solution is now heated in a water bath to 50° ; the conventional 10 per cent. solution of molybdate is added from a burette with constant stirring, 50 c.c. being added in five minutes. After about 10 c.c. in excess has been added, the heating is continued for 10 minutes, and the precipitate is collected on a weighed filter. It is advisable to test the filtrate with some more of the reagent, to make sure of the complete absence of phosphoric acid. The precipitate is washed first with water containing 1 per cent. of nitric acid, and finally once with distilled water. After removing the excess of moisture by means of blotting-paper, the filter is dried at 105° to constant weight. The process may also be used in presence of ammonium citrate, but the liquid should then be first largely diluted, and heated for 40 minutes at 65° . L. DE K.

Three new Reagents for Nitrites. By GEORGES DENIGÈS (*J. Pharm.*, 1895, [6], **2**, 289—293).—The first of these gives a reaction characteristic for nitrites, and is a modification of Millon's reagent; two solutions are employed. (A) 1 gram of pure white phenol is agitated with 4 c.c. of sulphuric acid and 100 c.c. of water. (B) Either 5 grams of pulverised mercuric acetate (or 3·5 grams of mercuric oxide and 20 c.c. of glacial acetic acid) and 100 c.c. of water, are mixed, shaken some minutes, treated with 0·5 c.c. of sulphuric acid, and filtered. A solution of acid mercuric sulphate may be used instead of B. Equal volumes of the two solutions are mixed, heated to boiling, and the solution, or potable water to be tested, added; when as much as 5 parts per 10,000 of nitrite is present, a red or pink coloration is obtained immediately with a drop or two in 4 c.c. of the mixed reagents; with more dilute solutions, 1 to 10 c.c. is required, and the boiling must be repeated; in this way 10 c.c. of a solution containing 2 per million of nitrite will yield a pink coloration in 4 c.c. of the mixed reagents; whilst with 10 c.c. of each reagent and 100 c.c. of water, and boiling for two or three minutes, 2 parts per ten million of nitrite can be detected. The solutions are colourless, stable, and are not affected by light, air, or oxidising agents; moreover, with the more dilute solution, the intensity of coloration is proportional to the quantity of nitrite present, and the tests may consequently be made quantitative.

The second reagent consists of 2 c.c. of aniline and 40 c.c. of glacial acetic acid, made up to 100 c.c. with water, boiled to destroy

any coloration, and then stored in a yellow or black glass bottle to keep it colourless. 5 c.c. is boiled with a drop to 10 c.c. of the suspected liquid, and gives a straw yellow to deep orange coloration, according as the quantity of nitrite present is small or great. The coloration is changed to red by hydrochloric or sulphuric acid, but is restored by neutralising with soda or sodium acetate. The red coloration is more delicate than the yellow, and as little as 2 parts per ten million of nitrous acid can be detected by using 50 c.c. of reagent to 100 c.c. of a potable water, boiling three or four minutes, and acidifying with sulphuric acid. Acid solutions should be neutralised with an alkaline hydroxide or carbonate before adding the aniline acetate. This reagent is affected by hypochlorites, hypobromites, and free chlorine and bromine, but not by chlorates or nitrates; it serves for the detection of nitrites in the presence of iodides, and for the ready determination of the former volumetrically.

The third reagent is the solution of resorcinol, which the author has suggested for the detection of tartaric acid (this vol., ii, 80); it contains 1 gram of pure white resorcinol, 100 c.c. of water, and 10 drops of sulphuric acid. By agitating 5 drops of this reagent with 2 c.c. of pure sulphuric acid and 4 drops of the solution under examination, an intense reddish carmine or violet-blue coloration is produced, without heating, even when only 0.00001 gram of nitrous acid is present per litre. This reagent is coloured green by chlorates.

D. A. L.

Estimation of Boric acid. By LEONCE BARTHE (*J. Pharm.*, 1895, [6], 2, 345–347).—Volumetric estimations of boric acid under the ordinary circumstances with the usual indicators are unsatisfactory; the author finds that in the presence of glycerol, and by the use of extract of hollyhock and phenolphthaleïn as indicators, the alkali and the boric acid of alkali borates can be titrated separately; with boric acid only in solution the matter is simplified, for, after adding glycerol and water, N/10 potash is used with these indicators. The tincture or extract of hollyhock is prepared as required by macerating the petals for some minutes; its reddish colour is turned bright red by acids, and green by alkalis; the latter change is very sharp, and alone is used in the method, which is best conducted in very dilute solutions. The results of Jay and Dupasquier (this vol., ii, 76) are criticised.

D. A. L.

Estimation of Carbonic Anhydride by Absorption. By HEINRICH HEIDENHAIN (*J. Amer. Chem. Soc.*, 1896, 18, 1–7).—The apparatus consists of an eprouvette filled with soda-lime with a little cotton-wool at the top, a cock to regulate the air current, and a capillary tube to offer resistance to the air in case the cock is opened too far. The air then passes through a funnel tube closed at the bottom by a perforated rubber stopper, into which the glass tube conveying the air is fitted. This arrangement in connection with the cock is a substitute for a three-way cock, but has the advantage that the regulating part does not get wet and is not exposed to heat. The funnel is filled with dilute acid, and its tube reaches to the bottom of a 300 c.c. evolution flask, which contains the weighed carbonate, and

is heated by a small burner. To prevent undue accumulation of water vapour, the steam is condensed by passing through an upward bent tube, around which a lead pipe conveying water is wound, which causes the steam to condense and run back into the flask. The gas then passes through a calcium chloride tube, then through a layer of pumice stone moistened with copper sulphate and then again through calcium chloride. The absorption tubes consist of two stoppered U-tubes containing soda-lime. The first tube contains a little calcium chloride at the end where the air enters, but the second tube is filled half with soda-lime and half with calcium chloride where the air leaves it.

The air is drawn by an aspirator, and a safety bottle and a guard tube containing soda-lime and calcium chloride prevent any moisture or carbonic anhydride from re-entering.

L. DE K.

Estimation and Separation of Copper. By F. MAWROW and WILHELM MUTHMANN (*Zeit. anorg. Chem.*, 1896, ii, 268—271).—When a solution of copper sulphate is treated with hypophosphorous acid at 60°, a yellowish-red precipitate of copper hydride is obtained, which, when heated at a higher temperature, is decomposed with formation of copper and hydrogen. This reaction is employed for the estimation of copper; the copper salt, previously converted into sulphate, is boiled with hypophosphorous acid as long as hydrogen is evolved, and the precipitated metal, which is extremely easy to collect, is washed with boiling water, alcohol, and ether, dried at 100°, and weighed. The results are very accurate. The nitrate or acetate can also be employed: but the solution must be free from chloride, as in this case cuprous chloride is formed, which is not further reduced by the hypophosphorous acid.

The method is especially applicable to the separation of copper from cadmium or zinc. The copper precipitate, which is quite free from cadmium or zinc, is filtered off and weighed as above, and the cadmium or zinc precipitated as sulphide from the filtrate.

Hypophosphorous acid is easily prepared by the action of phosphorous on barium hydroxide, and decomposition of the barium hypophosphite with sulphuric acid.

E. C. R.

Electrolytic Method for Estimating Mercury in Cinnabar. By W. B. RISING and VICTOR LIENHER (*J. Amer. Chem. Soc.*, 1896, 18, 96—98).—The authors dissolve the finely powdered mineral in dilute hydrobromic acid (1 part of 49 per cent. acid and 4 parts of water). The slight excess of acid is neutralised with aqueous potash, and after adding excess of potassium cyanide, the solution is electrolysed by a current giving 0.025 ampère, N.D.₁₀₀.

The hydrobromic acid is easily prepared by heating potassium bromide with sulphuric acid of 1.636 sp. gr., and passing the gas into water. On account of the low temperature at which it decomposes cinnabar, no loss by volatilisation of mercury takes place.

L. DE K.

Analysis of Aluminium and its Alloys. By HENRI MOISSAN (*Compt. rend.*, 1895, 121, 851—856).—In the absence of copper, about 3 grams of metal are dissolved in dilute hydrochloric acid, any

insoluble residue being decomposed by means of fused sodium carbonate, dissolved in acid, and mixed with the rest of the liquid, which is then evaporated to dryness, and dried at 125° until hydrogen chloride is no longer given off. The silica is estimated in the usual way; the solution is diluted to 500 c.c., and in 25 c.c. of this, the iron and aluminium are precipitated by ammonium sulphide in presence of a somewhat large quantity of ammonium salts and very little ammonia, and weighed as oxides. In order to estimate the iron, 250 c.c. of the filtrate from the silica is concentrated to about 100 c.c., and precipitated with excess of potassium hydroxide free from silica, the washed precipitate being redissolved in hydrochloric acid, and reprecipitated.

The estimation of sodium is based on the fact that aluminium nitrate is decomposed at a temperature at which sodium nitrate undergoes no change. 5 grams of aluminium is dissolved in nitric acid diluted with its own volume of water, care being taken that the temperature does not rise too high; after evaporation to dryness, the residue is heated at a temperature below the melting point of sodium nitrate until nitrogen oxides are no longer given off. The residue is extracted with water, and the solution slightly acidified with nitric acid and evaporated to dryness, the second residue extracted repeatedly with boiling water, the solution evaporated to dryness, redissolved, filtered, the sodium nitrate converted into chloride, and the chlorine estimated after drying at 300° .

Carbon is estimated by triturating 2 grams of the metal with 10 to 15 grams of mercuric chloride and a small quantity of water, evaporating the mixture on a water bath, and heating the residue in a current of pure hydrogen. The residue is then heated to redness in a current of oxygen, and the carbonic anhydride collected and weighed in the usual manner.

If the alloy contains copper up to about 6 per cent., 0.5 gram is dissolved in nitric acid free from chlorine, diluted to 50 c.c., and the copper deposited by electrolysis with a current of about 0.1 ampère, the process requiring about six hours at 60° , and 24 hours at the ordinary temperature. After removal of the copper, the aluminium, iron, and silicon are estimated in the manner already described.

A sample of aluminium from Pittsburg had the composition Al, 98.82; Fe, 0.27; Si, 0.15; Cu, 0.35; Na, 0.10; C, 0.41; N, traces; Ti, traces; S, absent, = 100.10. During the last few years, great progress has been made in the preparation of pure aluminium on a large scale. The industrial value of the metal cannot, however, be deduced from its composition alone, but physical tests must also be made.

C. H. B.

Volumetric Estimation of Manganese. By GEORGE AUCHY (*J. Amer. Chem. Soc.*, 1895, **17**, 943—947).—The author uses Volhard's process for estimating manganese in samples of steel, but in order to get trustworthy results, the following details should be adhered to.

3.3 grams of the sample is dissolved in a covered evaporating dish in 40 c.c. of 50 per cent. nitric acid, and 8 c.c. of strong sulphuric acid is then added. If, on evaporating, there is a tendency to bumping or spattering, some hydrochloric acid should be added. When

the mass becomes pasty and nearly dry, it is allowed to slightly cool, and is then boiled with water for a few minutes. When cold, the liquid is introduced into a 500 c.c. flask, nearly neutralised with sodium carbonate, and the iron precipitated by adding a sufficiency of emulsion of zinc oxide. After diluting to the mark and filtering, 250 c.c. of the filtrate is boiled in a 500 c.c. Erlenmeyer flask and titrated with standard permanganate (strength, 0.0055) until the supernatant liquid turns a rose colour no longer changing to yellow after shaking well. If the percentage of manganese is approximately known, it is better to add the greater part of the permanganate at once.

The number of c.c. of permanganate, divided by 10, equals the percentage of manganese in the sample.

L. DE K.

Detection of Chromates and Arsenites. By N. TARUGI (*Gazetta*, 1895, 25, ii, 248—251).—If a chromate and an arsenite are present together in a solution, usually only one of them is found in the liquid after boiling with sodium carbonate to remove the bases; this is owing to the formation of insoluble chromium arsenate. If the solution is heated for a short time only with sodium carbonate, both acids may be detected in the filtrate by adding silver nitrate after acidifying, as the precipitation of the chromium arsenate is not instantaneous.

W. J. P.

Niobium and Tantalum. By MARY ENGLE PENNINGTON (*J. Amer. Chem. Soc.*, 1896, 18, 38—67).—See this vol., ii, 305.

Estimation of Nitrites in Potable Waters. By AUGUSTUS H. GILL and HERBERT A. RICHARDSON (*J. Amer. Chem. Soc.*, 1896, 18, 21—23).—When testing peaty waters by Trommsdorff's iodo-zinc starch test, or by Griess' α -naphthylamine reaction, it is necessary to first remove the peaty matter, as this greatly interferes with the delicacy of these tests. For this purpose the authors recommend shaking 250 c.c. of the sample with 3 c.c. of an emulsion of alumina and filtering through a well-washed filter.

The reagents must, of course, be dissolved in water absolutely free from nitrites. This is best prepared by distilling water with alkaline permanganate, and collecting the middle portion only.

L. DE K.

The Colouring Matter of Natural Waters. Its Source, Composition, and Estimation. By ELLEN H. RICHARDS and J. W. ELLMS (*J. Amer. Chem. Soc.*, 1896, 18, 63—81).—The colouring matter of surface waters is derived from decaying leaves and consists of several complex substances such as tannins, glucosides, and their derivatives, &c. Iron, although generally present in very small quantity, is not an essential constituent. Some of the components are no doubt nitrogenous, as highly-coloured waters generally yield an abundance of albuminoid ammonia, but a large diminution of nitrogen does not cause a corresponding decrease in colour.

The actual amount of organic colouring matter cannot be estimated with anything like accuracy, but the authors have found that it is

comparatively easy to estimate the relative proportion of colouring matter in different samples. The nature of the colouring being practically the same, the relative amount may be ascertained colorimetrically. The standard sample is prepared by diluting a highly coloured water with distilled water, and comparing this with the colour produced by Nessler's reagent in a solution of ammonia of known strength. The standard water keeps fairly well for about six months, if sterilised at first. The colorimeter used by the authors is the well-known Lovibond's tintometer.

L. DE K.

Microscopical Examination of Water. By WILLIAM J. DIBDIN (*Analyst*, 21, 2—5).—One litre (or less) of the sample is measured in a flask with a long narrow neck, which is then inverted over a funnel containing a hardened filter 3 in. in diameter. The mouth of the flask should be just inside the filter. When all the liquid has passed through, the deposit is rinsed by means of a jet of pure distilled water into the micro-filter.

This is made from a perfectly clean piece of combustion tube about 10 in. long by drawing it out in the middle to a capillary tube, the narrowest part of which should be something less than 2 mm. in diameter. It is cut with a file at the point at which the tube is exactly 2 mm. It is then made into a filter by charging the small end with a suitable porous medium prepared by mixing equal parts of powdered air-dried clay and *Kieselghur*, moistening, and working to a smooth paste. When the capillary tube is charged, the mixture is warmed and gradually heated to redness in a gas flame.

The liquid containing the deposit soon filters through the plug (in obstinate cases suction must be resorted to), and when only about $\frac{1}{2}$ in. of water remains, the height of the column of suspended matter is ascertained and recorded. After cutting off the capillary tube, the deposit may be easily loosened by touching it with a platinum wire, and it may then be subjected to a careful microscopical examination. By this method of manipulation, the author has found objectionable matter in samples of water which had been reported to be free from deposit. An exhaustive table is given.

L. DE K.

Estimation of Methane and Hydrogen by Explosion. By AUGUSTUS H. GILL and SAMUEL P. HUNT (*J. Amer. Chem. Soc.*, 1895. 17, 986—994).—The authors have thoroughly investigated the conditions necessary for the success of the explosion process.

It appears that the idea that pure methane may be readily prepared by heating sodium acetate with soda-lime is erroneous, as the gas thus obtained sometimes contains 10 per cent. of free hydrogen.

The method by one explosion is fairly accurate for the hydrogen, but as regards the methane the method by two successive explosions should be used.

When a mixture of hydrogen and methane is exploded with a quantity of oxygen insufficient for both, but more than sufficient for either, about 60 per cent. of the hydrogen, 25 per cent. of the methane and 50 per cent. of the oxygen is consumed.

L. DE K.

Effect of adding Alum to Wine. By FAUSTO SESTINI (*Gazzetta*, 1895, 25, ii, 257—263).—The practice of adding small quantities of alum to wine is found to cause a gradual deposition, which consists principally of calcium phosphate; wine to which alum has been added would therefore not contain a high percentage of aluminium or phosphoric acid, but a relatively large proportion of sulphates. The custom of adding alum to wine is consequently injurious.

W. J. P.

Analyses of Fruit Sugars, Syrups, and Preserves. By PY (*J. Pharm.*, 1895, [6], 2, 488—491).—Polarising before and after inversion, as also the Fehling test, show that sugars from currants, cherries, and strawberries are similar to mixtures of 92 per cent. of saccharose with not more than 8 per cent. of glucose. Syrups contain about 60 per cent. of total sugar, of which about 4·8, at the highest, is due to fruit sugar, so that the amount of glucose present if the syrup or preserve is made with saccharose is negligible, and the purity of such syrup or preserve can be ascertained by making one Fehling test and one polariscopic examination. These are made in solutions containing 25 grams of the syrup or preserve in 100 c.c., decolorised by lead subacetate, and inverted by 10 per cent. hydrochloric acid. The saccharometric deviation at 17° should be within a few degrees of that indicated by multiplying the weight of the reducing sugars by 2·066; if otherwise, glucose must be sought in the usual way. Instead of the Fehling test, &c., a polariscope reading may be taken before and after inversion; if the rotation is still to the right in the latter case, there is no doubt that glucose is present, except in the case of plums. In fact, as much as 29 per cent. of glucose may be present and the rotation still be slightly to the left, therefore the two polarisings should not alone be depended on when the deviations are not well marked. Artificial fruit syrups consist of pure sugar, little or no fruit sugar, colouring matter, citric or tartaric acid; they should be tested for the colouring matter, the absence of fruit sugar ascertained, &c. Gelose can be detected in preserves by searching for diatoms, for example, *Grammatophora marina*, as well as by the presence of *Arachnoidiscus japonicus*.

D. A. L.

Estimation of Levulose in Honey and other Substances. By HARVEY W. WILEY (*J. Amer. Chem. Soc.*, 1896, 18, 81—90).—The process is based on the fact that the optical rotation of levulose is strongly diminished at an increased temperature, whilst the accompanying substances are scarcely affected. The most important part of the apparatus is a jacketed observation tube, which may be cooled to zero or heated to 88°, at which temperature a mixture of equal molecules of levulose and dextrose is optically inactive. In every case, the sugar solutions are made to standard volume at the temperatures at which they are to be read, thus avoiding variations due to expansion or contraction. In all cases, the observation tube should be left for at least half an hour in contact with the temperature controlling medium before the reading is made. Any variation in temperature produces a distortion of the field of vision, whilst a constant fixed temperature will disclose it in its true shape and distinctness of

outline. The strength of the sugar solution should be 26.048 grams of solid matter in 100 c.c. of liquid.

If K represents the deviation in divisions of cane sugar scale or in angular rotation produced by 1 gram of levulose for 1° temperature, T and t' the temperatures at which the observations are made, R the observed deviation in rotation, W the weight of levulose obtained, and L the percentage of levulose required, then

$$L = \frac{R}{K(T - t')} \div W. \quad \text{L. DE K.}$$

Estimation of the Extract of Malt in the Laboratory. By JOHN HERON (*J. Fed. Inst. Brewing*, 1895, 1, 116—118).—The author finds that the method described by him in 1888 (*J. Soc. Chem. Ind.*, 7, 267), although satisfactory for normal malts, yields results which are too low in the case of hard, steely malts. He therefore recommends that two determinations be made, one under the ordinary conditions and the other under conditions which yield what he terms the "highest available extract," and the nearer the results of the two methods approach one another the better is the quality of the malt under examination. The new method is carried out as follows:—50 grams of the malt, ground as fine as possible, is transferred to a 500-c.c. flask or beaker, and 400 c.c. of water at 55° added, giving an initial heat of 50° . The mash is carried on for an hour in a water bath, the temperature being gradually raised to 70° . It is then quickly raised to 88° , maintained at this temperature for 15 minutes and then cooled to 15.5° , made up to 515 c.c., filtered, and the extract determined in the usual way. A. K. M.

Estimation of Uric acid in Urine. By GOTTFRIED VON RITTER (*Zeit. physiol. Chem.*, 1895, 21, 288—296).—The method investigated is that of Hopkins (*Abstr.*, 1893, ii, 395), and, as further modified by that author, is stated to give good results. The urine is saturated with ammonium chloride; the precipitate of ammonium urate is washed, dissolved in concentrated sulphuric acid, and titrated with permanganate direct.

The paper is mainly concerned with details of manipulation.

W. D. H.

Composition and Analysis of Condensed Milk. By THOMAS HAMES PEARMAIN and CRESACRE GEORGE MOOR (*Analyst*, 20, 268—272).—The authors have analysed 50 brands of commercial condensed milk, and tabulated the results.

The analytical process used is as follows: 10 grams of the sample is diluted to 100 c.c.; 20 c.c. is evaporated in a platinum dish until the weight is constant, and finally burnt to ash. The proteids are estimated by evaporating 10 c.c. to dryness in a flask, and then treating by Kjeldahl's process. The milk sugar is estimated by diluting 10 c.c. with 50 c.c. of ammonia and 40 c.c. of water, and then using Pavy's process. The fat is estimated by applying Adam's paper process, working on 5 c.c. in duplicate. The fat may also be estimated by means of the Leffmann-Beam machine; but as it is necessary to dilute largely, the results are only approximate. L. DE K

Iodine Number of Lard. By LEOPOLD VAN ITALLIE (*Ned. Tydschr. Pharm., &c.*, 1895, **7**, 294—295).—The author has determined the iodine absorption of lards which he had himself prepared during a period of 12 months.

It appears that the iodine number is not influenced by the season; also that a sample, giving a figure slightly below 49, may still be genuine.

L. DE K.

Van de Moer's Reaction and the Detection of Cytisine. By K. GORTER (*Ned. Tydschr. Pharm., &c.*, 1895, **7**, 234—240, and *Arch. Pharm.*, 1895, **233**, 527—533).—Van de Moer was the first to suggest a delicate test for this alkaloid (*Abstr.*, 1891, 946); it consists in moistening the substance with ferric chloride and then with hydrogen peroxide; the red colour first disappears, but, on gently warming, a permanent blue coloration is developed; 0.05 milligram of the alkaloid may thus be detected.

The colour disappears on adding ammonia, but reappears on adding an acid. It has been stated that after the addition of soda the coloration does not return on acidifying; this, however, the author finds to be erroneous, as the colour, when discharged by aqueous soda or lime water, is completely restored by adding an acid.

The reaction is most delicate when the amount of iron present amounts to about half the weight of the cytisine, and it is probably owing to their having used too much ferric chloride solution that the test was condemned by Magelhaes and Partheil. The reaction recommended by these authors was warming the alkaloid with strong sulphuric acid and thymol, which causes first a yellow, then a red, and finally a claret-like colour. The author, however, states that this reaction is always given even in the complete absence of cytisine.

L. DE K.

Detection of Strychnine in a Medico-Legal Case. By MAKIEWICZ (*Arch. Pharm.*, 1895, **233**, 508—511).—An account of a controversy arising from the accumulation of the alkaloid in certain organs only of an exhumed body.

J. N. W.

A Delicate Test for Albumin in Urine. By ADOLF JOLLES (*Zeit. physiol. Chem.*, 1895, **21**, 306—310).—Acetic acid and potassium ferrocyanide will detect 1 part of albumin in 70,000 of urine. Its disadvantage is the production of an intense yellow colour due to nitrites in the urine (Karplus, *Centr. Klin. Med.*, **14**, 577). Spiegler's reagent (*Wien. Klin. Woch.*, 1892, No. 2) is not so sensitive, and its delicacy is diminished by a diminution of the urinary chlorides such as occurs in many diseases. The following reagent is recommended as the best, and it will detect the minutest traces (1 in 120,000) of albumin: mercuric chloride, 10, succinic acid, 20, sodium chloride, 10, water, 500 parts. Four or five c.c. of filtered urine are acidified with 1 c.c. of 30 per cent. acetic acid, and 4 c.c. of the reagent added; on shaking, if albumin is present, a precipitate occurs; a comparative test is made at the same time with 4—5 c.c. of the urine and 1 c.c. of acetic acid.

W. D. H.

General and Physical Chemistry.

The Influence of Electrolytic Dissociation, &c., on the Molecular Refraction. By MAX LE BLANC and P. ROHLAND (*Zeit. physikal. Chem.*, 1896, **19**, 261—286).—In order to determine whether the hydrogen ion has a greater specific refraction than that of the combined atom, the authors determined the difference between the molecular refractions of (1) weakly dissociated, (2) strongly dissociated, acids and their sodium salts, which are in all cases strongly dissociated. In the case of formic, acetic, glycollic, propionic, butyric, glyceric, and lactic acids, the difference in the molecular refractions varied between 3.08 and 3.72 (Gladstone), between 1.56 and 1.80 (Lorenz). For the more strongly dissociated acids, mono-, di-, and tri-chloroacetic, nitric, and hydrochloric acids, the differences were 3.17 to 1.37 and 1.60 to 0.75, the number decreasing with dilution and dissociation, so that the hydrogen ion exerts a greater influence than the acid ion. The refraction of sulphuric and tartaric acids were found by Hallwachs to remain almost constant on dilution, a result probably due to the influence of the other ions. Experiments with bases were undertaken, but no similar conclusion regarding the hydroxyl ions could be established. Assuming the acid ion to have the same equivalent refraction as in combination, and the hydrogen to have the atomic refraction 1.05, the values for sodium and chlorine were found to be 2.69 and 6.61. The latter agrees well with the value 6.42, which is independently obtained from the differences between the bases and chlorides. The refractions of salts in the solid state and in solution were also compared, that of the solution being usually greater, but in both cases the molecular refraction appears approximately additive. The experiments with various solvents indicate also a specific influence of the solvent.

L. M. J.

Absorption Spectra of some Chromothiocyanates. By GAETANO MAGNANINI (*Gazzetta*, 1895, **25**, ii, 373—379).—A study of the absorption spectra of some of the chromothiocyanates leads to results similar to those obtained by Magnanini and Bentivoglio (*Abstr.*, 1894, ii, 129) with the blue chromoxalates.

Cryoscopic and electrical conductivity determinations indicate that potassium chromothiocyanate is not a true double salt, but one which dissociates in aqueous solution into the ions K_3 and $Cr(CNS)_6$. A comparison of the photographed absorption spectra of three aqueous solutions containing gram molecules per litre of $K_3Cr(CNS)_6$, $Na_3Cr(CNS)_6$, and $Na_3Cr(CNS)_6 + 2NaNO_3$, shows that notwithstanding the diminution of the dissociation of the sodium salt brought about by adding sodium nitrate, the absorption spectra are identical.

W. J. P.

Absorption of Light by Solutions of Indophenols. By PIERRE H. BAYRAC and CH. CAMICHEL (*Compt. rend.*, 1896, **122**, 193—195).—Indophenols, although derived from phenols differing considerably in

composition, all show similar absorption spectra. The colour of the solution varies with the nature of the solvent, and the same solvent gives the same coloured solutions with different indophenols. The spectrum consists of a somewhat narrow, brilliant red band, and a broad and somewhat feeble green-blue and violet band, all the other rays being absorbed. As the concentration of the solution or the thickness of the absorbing layer increases, the middle of the red band seems to be displaced towards the blue end of the spectrum and *vice versa*. Notwithstanding the differences in the colours of the solutions, all the spectra are analogous, the differences being due to differences in the relative absorptions of the more refrangible and less refrangible halves of the spectrum.

Quantitative observations show that when equal volumes of the same solvent contain quantities of the indophenols proportional to their molecular weights, the red band occupies the same position in the various spectra.

It would seem that an examination of the character of the absorption spectrum may help to determine whether a particular substance is really an indophenol or not.

C. H. B.

Fluorescence of Sodium and Potassium Vapour, and its Importance in Astrophysics. By EILHARD WIEDEMANN and GERHARD C. SCHMIDT (*Ann. Phys. Chem.*, 1896, [2], 57, 447–453).—The authors find that both sodium and potassium vapour have a marked fluorescence, the first green, and the second red. The fluorescence spectrum of sodium vapour is composed of three parts, a continuous band in the red, a channeled band in the green, and the yellow sodium line. The fluorescence spectrum of potassium vapour consists of a red band, 695–615. The spectra which these vapours yield under the influence of electrical discharges appear to correspond to the fluorescence spectra, and Stokes' rule holds for these as for other cases of fluorescence. The authors point out that the establishment of fluorescence for the vapours of the metals would throw light on some hitherto unexplained astrophysical phenomena.

H. C.

Specific Rotation of α -Nitrocamphor in Various Solvents. By MOSÈ PESCIETTA (*Gazzetta*, 1895, 25, ii, 418–423).—Cazeneuve and van't Hoff have both remarked the extent to which the specific rotation of α -nitrocamphor is affected by variations in concentration and difference of solvent; the author has therefore determined the specific rotation of this substance in benzene and alcoholic solutions for the five wave-lengths given by the Landolt ray-filters.

The specific rotations $[\alpha]$ in a 1.064 per cent. benzene solution are -65.45° , -93.6° , -131.98° , -182.0° , and -294.3° , and for a 3.562 per cent. alcoholic solution $+2.64^\circ$, -2.30° , -13.11° , and -24.16° at 20° for the rays "red," D, "green," "light blue," and "dark blue" respectively (dark blue not given for alcoholic solution). A 1.2108 per cent. alcoholic solution at 20° is inactive to the ray "red," whilst a 10.754 per cent. solution is inactive to D. The dispersion coefficients are constant for the various concentrations in benzene solution. Both alcoholic and benzene solutions become more positive in specific rotation as the concentration increases.

The freezing point depressions of benzene and the rise in boiling point of alcohol caused by α -nitrocampbor are normal.

W. J. P.

Multitrotation of Reducing Sugars and of Isodulcitol. By CHARLES TANRET (*Compt. rend.*, 1896, **122**, 86—87).—See this vol, i, 334).

Acetylene as a Photometric Unit. By JULES VIOLE (*Compt. rend.*, 1896, **122**, 79—80).—When acetylene is burnt under a somewhat high pressure in a burner which produces a broad, thin flame, a very brilliant and remarkably white light, of constant intensity, is obtained, the illuminating power being practically uniform over a large area. By placing in front of the flame a screen pierced with an aperture or apertures of definite dimensions, very convenient photometric units can be obtained. The intensity of the flame is about 20 times that of the flame from an equal volume of coal gas burnt in an ordinary burner, and at least six times as great as that of the coal gas burnt in an incandescent burner.

In spectroscopic character, the light from the acetylene flame differs very little from that emitted by melting platinum.

C. H. B.

Dark Radiations. By GUSTAVE LE BON (*Compt. rend.*, 1896, **122**, 188—190).—When an ordinary negative is placed in contact with a sensitive plate, and a thin sheet of iron is put in front of the negative, the whole being enclosed in a printing frame and exposed to the light from a petroleum lamp for about three hours, a faint but distinct image is obtained on the sensitive plate, after prolonged energetic development. If a sheet of lead is placed behind the sensitive plate and the edges are wrapped over so that they come in contact with the iron in the front, other conditions remaining the same, a vigorous image is obtained on development. It is possible that the two metals produce thermo-electric currents, which add their effects to those of the dark radiations. The observed effects are not due to any appreciable rise of temperature. Exposure to sunlight gives similar results, the solar rays not being appreciably more active than those from a lamp. Cardboard and metals, especially iron and copper, are easily traversed by the rays. When plates similarly protected are exposed in a camera, they blacken on development, but yield no distinct images.

C. H. B.

Properties of Röntgen Rays. By JEAN PERRIN (*Compt. rend.*, 1896, **122**, 186—188).—Perrin has repeated some of Röntgen's experiments, and confirms his statements (1) that they produce developable images on ordinary photographic plates; (2) that they are not cathode rays; (3) that the opacity of the following substances to the rays increases from the beginning to the end of the list: carbon, bone, ivory, calcspar, glass, quartz, rock salt, sulphur, iron, steel, copper, brass, mercury, lead. Wood, paper, wax, paraffin, and water are very transparent; (4) that the propagation of the rays is rectilinear, but that they are not refrangible, are reflected only to a slight extent, and show no evidence of diffraction.

C. H. B.

Discharge Phenomena in Rarefied Metallic Vapours. By EILHARD WIEDEMANN and GERHARD C. SCHMIDT (*Ann. Phys. Chem.*, 1896, [2], 57, 454—458).—The authors show that rarefied metallic vapours contained in a heated glass vessel may be made to glow under the influence of oscillatory discharges. These vapours, even when the metal is known to be monatomic, then exhibit all the typical discharge phenomena, and the characteristic difference in the colour and spectrum of the anode and cathode discharge. The appearances observed with a number of the metals examined are described in the paper.

H. C.

Molecular Conductivity of Dilute Solutions. By NIKOLAI N. BEKETOFF (*J. Russ. Chem. Soc.*, 1894, 26, 65—66).—The known fact that the molecular conductivity of a solution of an electrolyte increases with dilution is explained by the author by an ingenious modification of Grötthaus' hypothesis. In the latter, the electrolysis of sodium chloride, for example, is supposed to proceed by the end-atom of sodium becoming detached and decomposing water to form sodium hydroxide, the end chlorine atom then uniting with the sodium of the next molecule, and so on to the other terminal, where the last chlorine atom is disengaged. This, however, does not explain the effect of dilution. The author's idea is that the intervening molecules of water take part more and more in the chain of reactions as the solution becomes more dilute, actually forming *free* sodium hydroxide and *free* hydrogen chloride in the intervals. As both caustic soda and free hydrogen chloride are better conductors than either sodium chloride or water, the rise of the mean molecular conductivity on dilution would be satisfactorily explained.

S. G. R.

Thermal Conductivity and Ion Velocity. By GEORG BREDIG (*Zeit. physikal. Chem.*, 1896, 19, 228—232).—The results obtained by the author for the kation velocity in the case of the amines (Abstr., 1894, ii, 226) are closely analogous to those obtained by Höfker (*Diss. Jena*, 1892) for the mean free path in these compounds in the gaseous state, the latter constant being obtained from measurements of the thermal conductivity of the gases. Both constants decrease with diminishing differences as the weight of the alkyl increases, and, in metameric amines, are greater the greater the number of alkyl groups united to the nitrogen. The author finds also that the thermal conductivity may be expressed as a linear function of the ion velocity, the observed and calculated numbers agreeing within the limits of experimental errors, as seen in the table, where the calculated values are obtained by the equation $K = 23.4 + 0.747\alpha$.

	Observed.	Calc.		Observed.	Calc.
Methylamine	66.4	66.5	Dimethylamine....	61.6	60.9
Ethylamine.....	58.4	58.4	Diethylamine.....	52.6	50.4
Propylamine....	52.6	53.4	Dipropylamine....	44.8	46.1
Butylamine.....	52.2	50.6	Trimethylamine...	57.1	58.6
Amylamine.....	49.0	48.8	Triethylamine....	46.8	47.8

L. M. J.

Specific Heats of Gases and Properties of Isothermals. By EMILE H. AMAGAT (*Compt. rend.*, 1896, **122**, 120—121).—Experiments made by Witkowski on the specific heat of air between 0° and -140° , and under pressures from 1 to 140 atmos., show that at low temperatures the variations in the coefficients for air become considerable, and these variations and the characters of the isothermals agree with those traced by the author for carbonic anhydride and for ethylene.

C. H. B.

Latent Heat of Evaporation of Benzene. By ERNEST H. GRIFFITHS and DOROTHY MARSHALL (*Phil. Mag.*, 1896, [5], **41**, 1—37).—The latent heat of evaporation of benzene has been determined by the authors, employing the method of experiment and the apparatus used by Griffiths in his determination of the latent heat of evaporation of water (*Phil. Mag.*, 1895, [5], **39**, 261—341). The latent heat of evaporation of benzene over the temperature range 20° to 50° (nitrogen scale) is represented by the equation

$$L = 107.05 - 0.158\theta,$$

where L is expressed in terms of a thermal unit at 15° . Assuming this formula to hold up to the normal boiling point of benzene, 80.2° , at this temperature L would be 94.37.

H. C.

Method of comparing directly the Heats of Evaporation of different Liquids at their Boiling Points. By DOROTHY MARSHALL and WILLIAM RAMSAY (*Phil. Mag.*, 1896, [5], **41**, 38—52).—The heats of evaporation of two liquids may be compared by raising the temperature of each to its boiling point (surrounding each vessel with a jacket of its own vapour), and then determining the loss of weight sustained by each vessel when a current of electricity is passed through a carbon filament immersed in the liquid. All other conditions being made the same for the two vessels, the ratio of their

	Ratio to benzene.	L.	t.	M.	$\frac{ML}{T}$.
Benzene	1.000	94.4	80.2	77.40	20.65
Toluene	0.920	86.8	110.8	91.30	20.61
Metaxylene	0.877	82.8	138.5	105.20	21.03
Water	—	536.6	100.0	17.86	25.64
Alcohol	2.293	216.5	78.2	45.66	28.09
Acetic acid	1.028	97.0	118.5	59.52	14.72
Methylic formate	1.167	110.1	31.8	59.52	21.45
Ethylic formate	1.000	94.4	54.3	73.42	21.13
Methylic acetate	1.028	97.0	57.1	73.42	21.53
Propylic formate	0.956	90.2	80.9	87.32	22.38
Ethylic acetate	0.933	88.1	77.15	87.32	21.93
Methylic propionate	0.943	89.0	79.7	87.32	21.99
Propylic acetate	0.881	83.2	101.25	101.22	22.45
Ethylic propionate	0.867	81.8	99.2	101.22	22.22
Methylic butyrate	0.814	79.7	102.7	101.22	21.43
Methylic isobutyrate	0.794	75.0	92.3	101.22	20.74

losses of weight should give the inverse ratio of the heats of evaporation of the liquids. Then, if the heat of evaporation of any one liquid is known, the absolute value of the heat of evaporation of any other liquid can be calculated from the ratio directly found.

The authors have been engaged in working out and perfecting the experimental details of this method of comparison, and, by adopting arrangements which are described in the paper, have been able to obtain satisfactory results. The latent heat of evaporation of benzene at the boiling point 80.2° , as determined by Griffiths and Marshall (preceding abstract), has been used as the standard of comparison.

The results obtained are given in the table on the preceding page.

H. C.

Strontium and Calcium Iodides. By TASSILLY (*Compt. rend.*, 1896, **122**, 82—84).—Strontium iodide crystallises at about 60° with 7 mols. H_2O , and attempts to obtain a hydrate with 6 mols. H_2O were unsuccessful. Heat of dissolution of $SrI_2 \cdot 7H_2O = -4.47$ Cal. Combining this with previous results

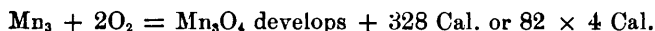
Sr solid + I_2 gas + $7H_2O$ liquid =	
$SrI_2 \cdot 7H_2O$	develops +158.07 Cal.
Sr solid + I_2 solid + $7H_2O$ liquid =	
$SrI_2 \cdot 7H_2O$	„ +147.27 „

Calcium iodide yields long needles of the hydrate $CaI_2 \cdot 8H_2O$. Heat of dissolution +1.735 Cal.

Ca solid + I_2 gas + $8H_2O$ liquid =	
$CaI_2 \cdot 8H_2O$	develops +144.47 Cal.
Ca solid + I_2 solid + $8H_2O$ liquid =	
$CaI_2 \cdot 8H_2O$	„ +133.67 „

C. H. B.

Heats of Formation of Manganese Compounds. By HENRY L. LE CHATELIER (*Compt. rend.*, 1896, **122**, 80—82).—The heats of formation were determined by burning the compounds in a calorimetric bomb with known weights of carbon and pure paper, the manganese, as a rule, being converted into the oxide Mn_3O_4 . The following results were obtained.



<i>Carbide</i> :— $Mn_3C + 3O_2 = Mn_3O_4 + CO_2$..	develops +412.4 Cal.
$Mn_3 + C$ (diamond) = Mn_3C	„ + 10.4 „
<i>Monoxide</i> :— $3MnO + O = Mn_3O_4$	„ + 55.2 „
$Mn + O = MnO$	„ + 90.8 „
<i>Peroxide</i> :— $3MnO_2 = Mn_3O_4 + O_2$	„ - 48.0 „
$MnO + O = MnO_2$	„ + 34.0 „
$Mn + O_2 = MnO_2$	„ +126.0 „
<i>Carbonate</i> :— $3MnCO_3 + O = Mn_3O_4 + 3CO_2$	„ - 27.8 „
$MnO + CO_2 = MnCO_3$	„ + 27.6 „
<i>Silicate</i> :— SiO_2 (quartz) + $MnO = MnO, SiO_2$	„ + 5.4 „

C. H. B.

Solubility of Gases. By DMITRI P. KONOWALOFF (*J. Russ. Chem. Soc.*, 1894, **26**, 48—49).—The author's experiments with a view to ascertain if the law of Dalton holds good in the case of dissolving carbonic anhydride in aniline, have shown that at two different temperatures, namely, 0° and 19·3°, the relation between the volumes of the dissolved gas and the observed pressure (which ranged between 600 and 900 mm.) remained constant.

A point of great interest is the examination of solutions of ammonia in water: these do not follow Dalton's law at temperatures near the ordinary, but approximate to it as the temperature increases, until at 100° the agreement is perfect.

Experiments as to the electric conductivity of ammonia solutions at higher temperatures led to results which are entirely opposed to electrolytic theories. The conductivity is directly proportional to the increase of temperature; the mean coefficient of increase between 18° and 100° being equal to about 2 per cent., a figure similar to that of salt solutions. At 95°, the conductivity is about three times what it is at 18°. The following are examples of the results.

Percentage of NH_3 .	3·10.		9·48.	
Temperature	18°	95°	18°	95°
Coefficient of conductivity	9·8	26·1	9·6	29·7

S. G. R.

Experimental Proof of the Laws of van't Hoff, Arrhenius, Ostwald, and Dalton for Dilute Solutions. By MEJER WILDERMANN (*Zeit. physikal. Chem.*, 1896, **19**, 233—250).—The values previously obtained by the author for the van't Hoff constant were 1·84—1·85, and as the experiments were performed with a convergence temperature above the freezing point the experiments were repeated under the reversed condition. The results, after all necessary corrections, were in good accord, and again gave values 1·84—1·85. The slight difference from the calculated value may be due to fundamental causes, or to an inaccurate thermometer scale, and experiments with resorcinol and cane sugar at another part of the thermometer scale gave the higher value 1·87. Experiments were made with sulphuric, dichloroacetic, trichloroacetic, and *o*-nitrobenzoic acids, and potassium chloride, to test the law of Arrhenius, and the values for the dissociation obtained from the freezing point and from the conductivity showed close agreement. The dilution law of Ostwald was tested in the case of dichloroacetic, *o*-nitrobenzoic, and trichloroacetic acids, the constancy of expression $\Delta^2 d / 1 - \Delta$ being satisfactory, and the variations actually occurring being irregular. Dalton's law, as applied to dilute solutions, was tested by mixtures of carbamide and resorcinol, carbamide and cane sugar, carbamide and dextrose, dextrose and aniline, and alcohol and carbamide. In all cases the law was found applicable, but the carbamide-resorcinol experiments are alone recorded. The non-influence of a non-electrolyte on the dissociation, and the decrease of the latter by the presence

of a similar ion have been also proved, but the publication of the complete results is postponed.

(See also Abstr., 1895, ii, 105; this vol., ii, 290.)

L. M. J.

Electrolytic Dissociation in Formic acid Solutions. By HUGO ZANNINOVICH-TESSARIN (*Zeit. physikal. Chem.*, 1896, 19, 251—260).—Nernst, having shown that the dissociating power of a solvent appears to be intimately connected with its dielectric constant (Abstr., 1894, ii, 266), the author undertook the determination of the degree of dissociation of solutions in formic acid, as this compound is distinguished by a very high dielectric constant ($K = 62.0$). The salts employed were lithium chloride, chlorides and bromides of sodium, potassium, and ammonium, hydrochloric, acetic, and trichloroacetic acids, the freezing point method being employed for the determinations. The salts in all cases exhibited strong dissociation, but the acids acted practically as non-electrolytes, hydrogen chloride apparently forming double molecules. Lithium chloride also appears to form double molecules in acetic acid solutions, whilst the order of the dissociation degree differs in these two solvents. Conductivity experiments are attended with more difficulty, owing to the conductivity of the acid itself, due probably either to true dissociation or to the presence of water. Potassium and sodium chlorides, hydrochloric and trichloroacetic acids, however, gave results in accord with the cryoscopic experiments.

L. M. J.

Freezing Points of Dilute Solutions. By WALTHER NERNST and RICHARD ABEGG (*Phil. Mag.*, 1896, [5], 41, 196—199; compare Abstr., 1895, ii, 155).—A reply to Jones' criticism (this vol., ii, 155) of the authors' results.

H. C.

Freezing Points of Dilute Aqueous Solutions. By E. H. LOOMIS (*Ann. Phys. Chem.*, 1896, [2], 57, 495—520).—Making use of the method described in a former paper (Abstr., 1894, ii, 228), the author has determined the freezing points of a number of dilute aqueous solutions, taking great precautions to ensure the highest degree of accuracy. The only alteration made in the apparatus previously used was the substitution of a freezing-point tube of 200 c.c. capacity for the 70-c.c. tube formerly employed. In each case the specific gravity and the conductivity of the solution employed were also measured. The substances examined were hydrochloric and phosphoric acids, the chlorides of potassium, ammonium, barium, and magnesium, the nitrates of potassium, sodium, and ammonium, and the sulphates and carbonates of potassium and sodium. The results obtained are given in tabular and curve form.

In these solutions, as in those of the other electrolytes which were formerly examined, the molecular reduction of the freezing point is found to increase continuously with rising dilution. The only exceptions to this rule are afforded by magnesium chloride and hydrochloric acid, in solutions of which the molecular reduction attains a *minimum* value when the concentration is about 1/10 gram mol. per litre. The molecular reduction for salts of monobasic acids and

radicles differs considerably in amount from that of salts containing dibasic radicles, and the increase which takes place on rising dilution is relatively more marked in the case of salts of the latter type. The results are extremely regular, and, when plotted in curve form, show no breaks or sudden changes of curvature.

The amount of electrolytic dissociation was calculated from the results for the solutions examined and compared with that calculated from the conductivities. With few exceptions, a striking agreement was observed, particularly in the cases of potassium chloride and sulphate. The differences are, however, in some cases greater than could be accounted for by experimental error, more particularly with the more concentrated solutions. It is also noticeable that although, according to the dissociation theory, the potassium salts should have a greater molecular reduction than the sodium salts in all cases, with the exception of the carbonates, the reverse was observed.

H. C.

Determination of the Freezing Points of Dilute Solutions.

By E. H. LOOMIS (*Ann. Phys. Chem.*, 1896, [2], 57, 521—532).—The author replies to objections raised by Jones, Wildermann, and others to his method of determining freezing points (*Abstr.*, 1894, ii, 228; 1895, ii, 7, 105).

H. C.

Solubility at the Solidifying Point of the Solvent.

By HENRYK ARCTOWSKI (*Zeit. anorg. Chem.*, 1896, 11, 272—277).—The author has determined the solubilities of sulphur, bromine, iodine, mercuric iodide, and tin tetriodide in carbon bisulphide, and of iodine in benzene, chloroform, and ether, at temperatures close to the solidifying point of the solvents. The results lead to the conclusion that the solubility curve may be prolonged beyond the point of solidification of the solvent, and that this point has no peculiar significance on the curve. It appears probable that no substance is completely insoluble in one of its solvents at the solidifying point of the solvent.

H. C.

The Polythionates. By HANS HERTLEIN (*Zeit. physikal. Chem.*, 1896, 19, 287—317).—The methods of preparation and purification for the polythionic acids and their potassium salts are first given, after which the observations of the physical properties are recorded. The molecular volume is found to increase regularly from the dithionates to the pentathionates, the differences being 12·75, 14·35, and 12·45 (calc.). The conductivity was determined by Kohlrausch's method, and the velocity of the acid ion calculated. In the case of the dithionates, the values thus obtained from the potassium, sodium, barium, and thallium salts were not in accord, the mean of the potassium and sodium results being 85. The velocity decreases with the addition of sulphur, thus $\frac{1}{2}\text{S}_2\text{O}_6$, 85; $\frac{1}{2}\text{S}_3\text{O}_6$, 72·8; $\frac{1}{2}\text{S}_4\text{O}_6$, 67·4; $\frac{1}{2}\text{S}_5\text{O}_6$, 61·4. Both dithionic and tetrathionic acids are found to be strong acids, the degree of dissociation at $v = 43\cdot18$ being respectively 0·896 and 0·92. The internal friction was determined by the method described by Ostwald, and was found to increase with increase in the sulphur content. The determinations of the molecular

refraction were made with a Pulfrich's refractometer with the following results for sodium light at 20°.

	I.	II.	Diff. I.	Diff. II.
Potassium dithionate	50·24	29·71	14·45	8·44
„ trithionate	64·69	38·15	14·70	8·53
„ tetrathionate.....	79·39	46·68	15·53	9·04
„ pentathionate.....	94·92	55·72		

The values in (I) and (II) are calculated by Gladstone's and Lorenz' formulæ respectively, and from these it appears that the sulphur is present in all the compounds in the bivalent state. Observations of the molecular volume in solutions were made, and also determinations of the electromotive force with different electrodes, the latter experiments indicating that the metal is not directly united to sulphur. The author considers the physical properties of the compounds to accord best with the constitutional formulæ proposed by Mendeléeff (*Principles of Chemistry*). L. M. J.

Molecular Solution Volumes and Molecular Volumes of Organic Compounds. By ISIDOR TRAUBE (*Annalen*, 1896, 290, 43—122; compare Abstr., 1895, ii, 70 and 209).—The author brings forward the experimental details on which are based the conclusions already indicated (this vol., ii, 152).

In addition to the points noticed (*loc. cit.*), it is observed that the molecular solution volume is not only additive and constitutive in character, but also configurative, the volumes of crotonic, dibromocrotonic, allocinnamic, allofurfuracrylic, maleic, and citraconic acids being appreciably smaller than those of the trans-modifications; differences also occur between the molecular solution volumes of ortho-compounds and the values obtained for the meta- and para-isomerides.

The property of polyesterism (Abstr., 1895, ii, 71) is exhibited by nitrogen, phosphorus, chlorine, bromine, and iodine, and it is found that in monhalogenised acids the three last-named elements have an atomic solution volume = 13·2 c.c., and, therefore, identical with the value for cyanogen. The author's results indicate the quinquavalence of nitrogen in nitro-groups, and evidence is adduced in favour of ring structure in amido-acids. M. O. F.

Velocity of Reaction between Ethylic Iodide and Silver Nitrate in Ethylic and Methylic Alcohols. By V. CHIMINELLO (*Gazzetta*, 1895, 25, ii, 410—418).—The author has determined the velocity of reaction between ethylic iodide and silver nitrate in ethylic and methylic alcohol solutions at 0°, 10°, and 15° for different times; action was arrested by pouring the mixture into water, and the unchanged silver nitrate was titrated with thiocyanate.

In ethylic alcohol at 0°, the reaction is of the first order, the velocity coefficient *AK* being 0·0188 and 0·0143 at 5 and 180 minutes respec-

tively, so that at this temperature action probably proceeds in accordance with the equation $\text{EtI} + \text{AgNO}_3 = \text{AgI} + \text{EtNO}_3$.

At higher temperatures, the velocity coefficient diminishes considerably as the time increases; thus at 10° the values of k for 2 and 90 minutes are 0.0639 and 0.0251 respectively, indicating that secondary action occurs at temperatures above 0° ; the secondary action, perhaps, proceeds in accordance with the equation given by Bertrand, $\text{C}_2\text{H}_5\cdot\text{NO}_3 + \text{C}_2\text{H}_5\cdot\text{OH} = \text{C}_2\text{H}_5\cdot\text{NO}_2 + \text{CH}_3\cdot\text{CHO} + \text{H}_2\text{O}$; the author was only able to detect in the liquid ethylic nitrite and acetic acid, the oxidation product of the acetaldehyde produced.

The velocity coefficients in methylic alcohol decrease continuously as the time increases, being at 0° , 0.0660 and 0.0248 at 2 and 100 minutes respectively; the considerable rise in the velocity coefficients attending the change of solvent is evidently due to the general accelerating effect of methylic alcohol, whilst the gradual diminution of the coefficient as the time increases, is probably caused by secondary action, according to the equation $\text{EtI} + \text{MeOH} = \text{MeI} + \text{EtOH}$.

W. J. P.

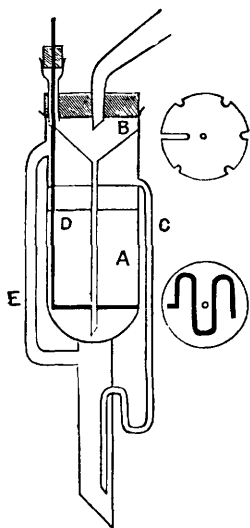
Function corresponding with the Periodicity of the Properties of the Elements. By FLAVIAN M. FLAVITZKY (*Zeit. anorg. Chem.*, 1896, 11, 264—267).—The relationship of the properties of the elements to their atomic weights may be expressed by the formula $\alpha \cot 2\pi\phi(p)$, where α is a constant dependent on the property under discussion, and $\phi(p)$ is a function of the atomic weight p . This formula, which was proposed by the author in 1887, is practically identical with that recently put forward by Thomsen (this vol., ii, 16).

H. C.

Eutropic Series. By W. ORTLOFF (*Zeit. physikal. Chem.*, 1896, 19, 201—227).—From the examination of the known physical constants of the metals beryllium, magnesium, zinc, cadmium, mercury, iron, cobalt, and nickel, and of a large number of their compounds, the author shows that they fall into two eutropic series, that is, series in which not only the physical properties, but also the crystallographic constants exhibit a regular variation. In the first series, consisting of the compounds of the first five metals, the increase of molecular weight is generally associated with an increase in specific gravity, molecular volume, index of refraction and molecular refraction, but a decrease in the hardness and specific heat. In the second series, with increasing molecular weight is associated an increasing index of refraction and specific gravity, but a decreasing molecular volume, molecular refraction, and hardness. In both series, in the monoclinic compounds, the α -axis decreases and the c -axis increases with increasing molecular weight, whilst in the hexagonal compounds, the c -axis increases in the first series but decreases in the second. Exceptions in this respect are usually associated with other anomalies in the physical properties of the compound.

L. M. J.

Extraction Apparatus for Liquids. By A. KURBATOFF (*J. Russ. Chem. Soc.*, 1894, 26, 39—40).—A modification of the ordinary



Soxhlet apparatus. The vapour of the solvent enters the condenser through the tube E, and after condensation drops into the funnel B, passes to the bottom of the cylinder A, and, being lighter than the liquid to be extracted, rises through it and flows down into the recipient through the tube C. A little agitator D, is suitably arranged in the cylinder A, and proves very useful in certain cases, such as milk.

Results obtained by this apparatus have been found to be in perfect accordance with those obtained in Soxhlet's apparatus.

S. G. R.

Lecture Experiment. Combustion of Oxygen in Ammonia, &c. By IWAN P. OSSIPOFF (*J. Russ. Chem. Soc.*, 1894, **26**, 55—56).—A beaker is about half filled with strong solution of ammonia, and the liquid moderately heated so as to replace the air in the beaker by ammonia. A slow current of oxygen is then passed into the

beaker through a tube which almost touches the surface of the liquid. A light is then brought near the beaker, and as soon as a flame appears at the end of the oxygen tube, the latter is quickly immersed in the liquid. Simultaneously the current of oxygen is increased, and instantly a whole sheaf of pale greenish flame will be seen above the liquid.

In connection with this experiment, it has been found that oxygen burns very well in paraffin oil and alcohol, and that lighting-gas burns in fuming nitric acid. The apparatus used is in all these cases the same as the above.

S. G. R.

Inorganic Chemistry.

Preparation of Hydrogen Bromide and Hydrogen Iodide.
By J. H. KASTLE and J. H. BULLOCK (*Amer. Chem. J.*, 1896, **18**, 105—111).—*Hydrogen Bromide*.—Bromine is allowed to flow slowly from a tap-funnel into a solution of naphthalene (15 to 20 grams) in a little orthoxylene. Hydrogen bromide is at once evolved, and is freed from bromine by passing through concentrated aqueous hydrobromic acid holding red phosphorus in suspension, and then through a U-tube containing red phosphorus; and from moisture by means of phosphoric anhydride. The flow of bromine once regulated, the evolution proceeds regularly. Petroleum boiling above 150° may be used instead of xylene. The yield of hydrogen bromide is 91 per cent. of the theoretical.

Hydrogen Iodide.—Ten grams of finely divided iodine are mixed with an equal bulk of finely powdered resin (colophony), and the whole with an equal bulk of white sand. The mixture is heated in a retort, the neck of which passes into a Woulff's bottle, where a brownish liquid condenses together with iodine, while hydrogen iodide passes on, and is freed from iodine by red phosphorus and from moisture by phosphoric anhydride; it is then perfectly colourless. Ten grams of iodine yielded 5.4 grams of the acid. The method is very rapid, and well suited for lecture demonstrations.

A. E.

Properties of Liquid Hydrogen Iodide. By R. S. NORRIS and F. G. COTTRELL (*Amer. Chem. J.*, 1896, **18**, 96—105).—The liquid was formed by passing dry hydrogen iodide into a stoppered tube surrounded by solid carbonic anhydride; the tube was then removed from the carbonic anhydride, the stopper being held in place by a clamp; the liquid could thus be kept at the temperature of the room for two or three hours before it all escaped. It is limpid and colourless. The solid, formed on freezing it, is heavier than the liquid, and resembles ice in appearance. Sunlight rapidly liberates iodine from the liquid, the action becoming less as the amount of free iodine in the solution increases. Silver, mercury, copper, tin, iron, aluminium, sodium, and potassium were attacked, giving iodides and liberating hydrogen; lead, bismuth, cadmium, antimony, zinc, magnesium, and thallium were not acted on. Of the above metals, liquid hydrogen chloride dissolves only aluminium (Gore, *Phil. Mag.*, 1865, [4], **29**, 541). Cupric oxide and manganese dioxide dissolved quickly, forming cuprous and manganous iodides. Dry sodium and calcium carbonates were quite unacted on. Sulphur gradually dissolved, forming hydrogen sulphide and liberating iodine. Carbon bisulphide merely dissolved. Water refuses to mix with the acid, and if shaken with it breaks into globules, which rise to the surface.

Liquefied gases were introduced in thin sealed tubes, which were broken by shaking. Chlorine, issuing from a small hole in the tube, liberated iodine, and, as the action became more energetic, burst into flame. Liquid cyanogen liberated iodine, forming hydrogen cyanide and a flocculent precipitate. Liquid sulphurous anhydride set free sulphur and iodine, and formed hydrogen sulphide. Liquid ammonia reacted violently forming ammonium iodide. Alcohol and ether both form ethylic iodide.

On the whole, liquid hydrogen iodide is more inert than the gas, and more active than liquid hydrogen chloride.

A. E.

Molecular Weight of Sulphur. By WILLIAM R. ORNDORFF and G. L. TERRASSE (*Amer. Chem. J.*, 1896, **18**, 173—207).—The molecular weight of sulphur in solution in toluene and in carbon bisulphide, as determined by the boiling point method, is in each case 288, corresponding with S_8 . The monoclinic and orthorhombic forms have therefore the same molecular weight.

As the result of a large number of experiments carried out in solutions of varying degrees of concentration, the following conclusions are arrived at.

(1) In solvents boiling below the melting point of sulphur, such as toluene, carbon bisulphide, and benzene, the sulphur molecule is represented by S_8 .

(2) In solvents boiling above the melting point of sulphur, such as metaxylene, phenol, and phenetol, the molecule corresponds with S_8 .

By solution in sulphur chloride this complex molecule is apparently dissociated, since, as a mean of 12 experiments conducted in this solvent, a molecular weight of 61.9 corresponding with S_2 was arrived at.

The authors have also made molecular weight determinations of this substance, by means of the depression in the freezing point, when dissolved in naphthalene and diphenyl, with a result in the former case of 224, corresponding with S_7 , and in the latter of 256 corresponding with S_8 . They, however, attach very little importance to these results, the cryohydrate temperatures of these solvents with sulphur lying so near their freezing points.

J. F. T.

Thionyl Bromide and Chlorobromide. By ADOLPHE BESSON (*Compt. rend.*, 1896, **122**, 320—322).—When dry hydrogen bromide is passed into thionyl chloride at a temperature not exceeding 100° , and the product is fractionated under reduced pressure, thionyl chlorobromide and bromide, and sulphur bromide are obtained.

Thionyl chlorobromide, $SOClBr$, is a pale yellow liquid which boils and slightly decomposes at about 115° under normal pressure, and does not solidify at -23° ; sp. gr. = 2.31 at 0° . At a temperature a little above its boiling point, it decomposes into sulphurous anhydride, thionyl chloride, bromine, and sulphur bromide, and the same decomposition takes place slowly in the cold. In contact with mercury, thionyl chloride and mercurous bromide are formed, sulphur is liberated and sulphurous anhydride is given off.

Thionyl bromide, $SOBr_2$, is an orange-yellow liquid which boils at about 68° under a pressure of 40 mm., and does not solidify at -23° ; sp. gr. = 2.61 at 0° . When heated, it decomposes rapidly into bromine, sulphur bromide, and sulphurous anhydride. In contact with mercury, it yields sulphur, sulphurous anhydride, and mercurous bromide. Thionyl bromide is not formed by the action of sulphurous anhydride on phosphorus pentabromide.

Both the chlorobromide and the bromide are rapidly decomposed by water.

C. H. B.

Action of Carbonic Chloride on some Hydrogen Compounds. By ADOLPHE BESSON (*Compt. rend.*, 1896, **122**, 140—142).—Phosphonium bromide acts slowly on carbonic chloride in the cold, but very rapidly at 50° , and in sealed tubes, the action is complete in a few hours. The products are hydrogen chloride, hydrogen bromide, and hydrogen phosphide, carbonic oxide, and solid yellow hydrogen phosphide.

Hydrogen iodide dissolves readily in carbonic chloride, but, even when cooled with ice and salt, there is a violent action, with libera-

tion of iodine. Phosphonium iodide reacts slowly with the chloride at 0° , and in sealed tubes between 0° and 10° , the action proceeds somewhat rapidly with production of hydrogen chloride, carbonic oxide, phosphorus iodide, P_2I_4 , and red phosphorus, which retains about 10 per cent. of iodine, seemingly in the form of a subiodide.

Hydrogen phosphide is practically without action on carbonic chloride; hydrogen sulphide acts at 200° under pressure with formation of sulphurous and carbonic anhydrides, and carbon oxysulphide; hydrogen selenide at 200° yields selenium, hydrogen chloride, and carbonic oxide, and at 230° the selenium acts on the excess of carbonic chloride with production of selenium chloride.

C. H. B.

Solubility of Sodium Thiosulphate in Alcohol. By F. PARMENTIER (*Compt. rend.*, 1896, **122**, 135—137).—The author has repeated Brunner's experiments with ordinary sodium thiosulphate (*Abstr.*, 1895, ii, 488), and also with the modification of the thiosulphate described by himself and Amat (*Abstr.*, 1884, 819). With absolute alcohol, the thiosulphate cannot be completely fused in sealed tubes even at 100° ; with alcohol of 80° , it melts at 41° and not at 47.9° , and with alcohol of 63° , at 33° . The salt superfused in presence of alcohol of 80° , solidifies in the allotropic modification when cooled with a mixture of ice and salt, but the product melts at 28° instead of 32° (*loc. cit.*). The determinations of solubility do not agree with those of Brunner, and show that, although the solubility of the crystallised thiosulphate is constant with the quantity of solvent (alcohol and water), the solubility of the superfused thiosulphate increases with the volume of the solvent. The concentration of the alcohol above the superfused salt also varies, and a complex condition of equilibrium is set up between the alcohol, the water, and the anhydrous salt.

C. H. B.

Sodium Sulpharsenate. By LE ROY W. MCCAY (*Zeit. anal. Chem.*, 1895, **34**, 725—730).—A feebly alkaline solution of sodium arsenate was saturated with hydrogen sulphide and heated in a closed flask. The cooled solution was then poured into alcohol, and the precipitated salt air-dried. Analyses, in which the arsenic pentasulphide, sodium, and water were all directly estimated, showed the composition to be $Na_3AsS_4 \cdot 8H_2O$, the numbers agreeing far less closely with the hitherto accepted formula $2Na_3AsS_4 \cdot 15H_2O$.

The author is unable to confirm Nilson's statements as to the existence of orthosulpharsenic acid, H_3AsS_4 . The precipitate obtained by adding a mineral acid to a dilute solution of the sulpharsenate consists of hydrated arsenic pentasulphide, with only traces of hydrogen sulphide, which are easily and completely removed by a current of hydrogen. The precipitate loses its water completely in a vacuum, or when dried at 87° .

M. J. S.

Lithium Hydride. By ANTOINE GUNTZ (*Compt. rend.*, 1896, **122**, 244—246).—Lithium combines somewhat rapidly with hydrogen at a dull red heat, but the conversion into hydride is incomplete. At a bright red heat, however, combination takes place with incandes-

cence, and the vapour of the lithium combines with the hydrogen to form a white solid hydride, LiH , which is deposited on the cool parts of the tube. It is not deliquescent, and alters very slowly when exposed to air, but is decomposed by water with formation of the hydroxide and liberation of hydrogen. When heated in nitrogen, it is converted into the nitride, and when heated in air, it burns and yields the oxide.

C. H. B.

Magnesium Silver Nitrite. By LEOPOLD SPIEGEL (*Chem. Zeit.*, 1895, **19**, 1423).—A solution of silver nitrite and magnesium nitrite in molecular proportion was boiled during a considerable time, filtered, when cool, from excess of silver salt, and evaporated to a syrupy consistency. After separation from the last traces of silver nitrite, the liquid was submitted to desiccation in a vacuum. The residue, which crystallised in glistening needles, was powdered, and dried until constant in weight. The aqueous solution, which quickly blackened on exposure to light, was decomposed with nitric acid and analysed. The results agreed with the formula



A. L.

Inertness of Alkaline Earths with respect to Hydrogen Chloride. By VICTOR H. VELEY (*Ber.*, 1896, **29**, 577—580).—Hydrogen chloride was dried by passing it in a slow stream through sulphuric acid, over phosphoric anhydride, and through a tube packed with pumice and freshly ignited lime (on which the dry gas has no action in the cold); it was then passed over the dry base that was to be experimented with. At the ordinary temperature, dry hydrogen chloride has no action on dry lime; at 40° there is a very slight action, and at 80° nearly half of the gas is absorbed, and water is seen to be formed. Magnesia reacts a little more readily, probably owing to its being in a state of finer division. Baryta reacts even at the ordinary temperature, but it is difficult to get it quite dry.

C. F. B.

Hydraulic Cements. By ORAZIO REBUFFAT (*Gazzetta*, 1895, **25**, ii, 481—393).—The author gives a summary and criticism of the work done by Le Chatelier and others on hydraulic cements during recent years.

W. J. P.

Preparation of Pure Strontium Compounds. By S. P. L. SÖRENSEN (*Zeit. anorg. Chem.*, 1896, **11**, 305—378).—The results of a large number of experiments show how difficult it is to separate strontium salts from calcium and barium salts; and that isomorphous salts are more difficult to separate than those which are not isomorphous. Thus, calcium chloride cannot be completely separated from strontium chloride by means of concentrated hydrochloric acid, although, when pure, they behave quite differently towards this reagent. Strontium and barium chlorides which are not isomorphous, although they behave in a similar manner towards concentrated hydrochloric acid, can be almost completely separated by this acid, whereby the greater portion of the barium chloride is precipitated without the slightest trace of strontium chloride. Strontium and barium nitrate cannot

be separated; calcium nitrate is, however, easily separated from the two preceding. The sulphates of calcium, strontium, and barium are isomorphous, and although they differ considerably in their solubility and stability towards alkali carbonates, it is impossible to separate them when precipitated together. The best method of preparing pure strontium salts is as follows. Commercial strontium carbonate (95 grams) is dissolved in the least possible quantity of hydrochloric acid, diluted to 400 c.c., and warmed until all the carbonic anhydride is expelled; 5 grams of solid strontium hydroxide is then added, the mixture shaken and warmed on the water bath, filtered, and the filtrate treated with 5—10 c.c. of chlorine water, again warmed, and filtered. By this treatment, any heavy metals which may be present are separated. The filtrate, which should be strongly alkaline, is treated with a slight excess of hydrochloric acid, diluted to 500 c.c., and treated with so much concentrated hydrochloric acid that, on cooling with cold water, a separation of needles takes place. After some time, the clear solution is decanted and the precipitated barium chloride washed with 25—30 per cent. hydrochloric acid, the wash-water being added to the main solution. The solution is then treated with concentrated sulphuric acid (70 grams) mixed with water (500 c.c.), and after remaining until the following day, the precipitated sulphates are separated, washed free from acid, and treated with 10 per cent. ammonium carbonate solution. The product is washed with warm water, and a small portion dissolved in nitric acid, when only a very small quantity of sulphate should remain undissolved; if much undissolved sulphate remains, the product must be again treated with ammonium carbonate. The washed product is then treated with a slight excess of nitric acid, filtered, mixed with 100 c.c. of 66 per cent. nitric acid, and then with 20 c.c. of dilute sulphuric acid (corresponding with about 2 grams SrO), and allowed to remain until the following day. The filtrate is successively treated in the same way with 10 c.c. additions of sulphuric acid until the precipitate is free from barium. The filtrate is now evaporated to dryness, the residue dissolved in water, filtered, evaporated to a pasty consistency, and mixed with 200—300 c.c. of alcohol. The precipitate is separated, washed with alcohol, and again dissolved in water and precipitated with alcohol until free from calcium. By this method 76—77 per cent. of the theoretical quantity of pure strontium salt is obtained.

The following method is employed for the detection of small quantities of calcium in strontium salts. The strontium nitrate (corresponding with 0.5 gram SrO) is dissolved in water and evaporated to complete dryness in a platinum dish; the dry residue is rubbed and well shaken with a small quantity of a mixture of ether and alcohol, the mixture filtered until quite clear, and the filtrate evaporated to dryness. The minute residue thus obtained is dissolved in nitric acid, mixed with ammonia, and treated in a test tube with ammoniacal arsenic acid, when, in the presence of lime, the salt $\text{Ca}(\text{NH}_4)\text{AsO}_4 + 7\text{H}_2\text{O}$, which is very characteristic when examined under the microscope, is precipitated. By this means 0.05 per cent. of calcium can be easily detected. If ammonium oxalate is employed

instead of ammonium arsenate, the presence of 0.03—0.04 per cent. of calcium gives a distinct precipitate, but this precipitate is not characteristic.

Small quantities of barium are detected as follows: The faintly acid solution of strontium nitrate or chloride (0.5 gram SrO) is diluted to 200 c.c., mixed with 5 c.c. of ammonium acetate solution (50 c.c. acetic acid (1 : 1), neutralised with ammonia and diluted to 100 c.c.), and then with 10 c.c. of ammonium chromate solution (1 gram ammonium chromate). The mixture is allowed to remain until the following day, and the precipitate washed with water, dissolved in dilute nitric acid, and mixed with ammonium acetate and ammonium chromate, when, in the presence of 0.033 per cent. of baryta in the strontium salt, a distinct turbidity is obtained. E. C. R.

Zinc Oxyiodides. By TASSILLY (*Compt. rend.*, 1896, **122**, 323—325).—When 20 grams of zinc iodide and 20 grams of water are heated in sealed tubes at 150° with 0.2 gram of zinc oxide, the oxyiodide, $\text{ZnI}_2 \cdot 9\text{ZnO} \cdot 24\text{H}_2\text{O}$, or $\text{ZnI}_2 \cdot 9\text{Zn}(\text{OH})_2 + 15\text{H}_2\text{O}$, is obtained in white, hexagonal lamellæ, which act on polarised light. If ammonia is added to a solution of zinc iodide in quantity insufficient to precipitate the whole of the zinc, the oxyiodide, $\text{ZnI}_2 \cdot 5\text{ZnO} \cdot 11\text{H}_2\text{O}$, is obtained in slender, microscopic needles.

The ammonio-zinc iodides, $\text{ZnI}_2 \cdot 4\text{NH}_3$, and $\text{ZnI}_2 \cdot 5\text{NH}_3$, yield only zinc oxide when treated with excess of water; when heated with a small quantity of water in sealed tubes, they both yield the compound $\text{ZnI}_2 \cdot 4\text{NH}_3$. The action of zinc oxide on ammonium iodide solution yields a crystalline compound, $3\text{ZnI}_2 \cdot 5\text{NH}_3 \cdot 3\text{H}_2\text{O}$, but this does not give an oxyiodide on treatment with water. C. H. B.

Silicides. By GUILLAME J. L. DE CHALMOT (*Amer. Chem. J.*, 1896, **18**, 95—96).—*Copper silicide* is obtained in flat, bluish white crystals, of sp. gr. 4.25, by heating sand and charcoal in an electric furnace in presence of copper. The crystals could not be obtained pure, but analyses indicate the formula Cu_2Si_3 . Aqua regia dissolves part of the copper, and silica is formed. A grey crystalline *silver silicide* was obtained by subjecting a mixture of sand, charcoal, lime, and silver to a current of 240 ampères and 25 volts. On boiling for 75 minutes with nitric acid, silica was formed, but only part of the silver was dissolved, indicating that the silver and silicon are in chemical combination. A. E.

Copper Silicide. By VIGOUROUX (*Compt. rend.*, 1896, **122**, 318—319).—Copper and silicon, when heated in a current of hydrogen in a reverberatory furnace, or the oxyhydrogen furnace, yield alloys which become whiter, harder, more brittle, and more resistant, as the proportion of silicon increases from 5 to 15 per cent., and it is only when it reaches 20 per cent. that the product becomes heterogeneous, crystalline, and very brittle.

When copper is heated with about 10 per cent. of silicon in the electric furnace until the excess of copper has volatilised, a definite silicide, SiCu_2 , is obtained as a very hard, brittle, steel-grey compound,

of sp. gr. 6.9 at 18°. It is attacked, with incandescence by fluorine in the cold, by chlorine below a red heat, and by bromine and iodine at higher temperatures. Moist air attacks it at the ordinary temperature, and dry air or oxygen converts it into a silicate below a red heat. It reduces water vapour, and is attacked by the haloïd hydracids at a red heat with production of a haloïd salt of copper and silicochloroform or analogous compounds. Acids attack it energetically, and fused alkali hydroxides or carbonates decompose it completely if it has been very finely powdered. C. H. B.

Action of Heat on Mercurous Iodide. By MAURICE FRANÇOIS (*Compt. rend.*, 1896, **122**, 190—193).—Mercurous iodide cannot be melted without decomposing, and, if heated in narrow tubes, mercury separates and sinks to the bottom, whilst a mixture of mercurous and mercuric iodides floats on it. At 300°, equilibrium is established when the supernatant mixture contains 36.5 per cent. of mercuric iodide and 63.5 per cent. of the mercurous salt, the limit being the same whether mercurous iodide or a mixture of mercury and mercuric iodide is heated. The dissociation is analogous to that produced by the action of a liquid on a solid.

When mercurous iodide is sublimed, the condensed product contains mercury and mercuric iodide, but a mixture of 2 mols. of mercuric iodide and 1 mol. of mercurous iodide will sublime without decomposing. A similar mixture can be melted without decomposition, and, if allowed to cool, deposits at first crystals of mercurous iodide only, which, however, always retain some of the mercuric salt mechanically.

It is obvious, from these results, that the numbers usually given for the melting and boiling points of mercurous iodide are erroneous.

C. H. B.

New Series of Metallic Ammonium Compounds. By O. FRITZ WIEDE and KARL A. HOFMANN (*Zeit. anorg. Chem.*, 1896, **11**, 379—384).—The salt, $\text{Co}_2\text{C}_2\text{S}_7 \cdot 6\text{NH}_3$, is obtained by passing nitric oxide through a mixture of freshly prepared cobaltous hydroxide, aqueous ammonia, and carbon bisulphide. The salt, which is mixed with an amorphous bye-product, is purified by washing with alcohol. It crystallises in black, lustrous rhombohedra, dissolves sparingly in water, yielding a yellowish-green solution, and is soluble in sodium hydroxide with a dark green coloration, at first without evolution of ammonia. It is decomposed by strong acids with precipitation of sulphur, and, when heated, gives off carbon bisulphide. By prolonged heating with sodium hydroxide, all the nitrogen is given off as ammonia. It can also be prepared by warming a mixture of cobalt hydroxide, ammonia, and carbon bisulphide.

The *nickel salt*, $\text{NiCS}_3 \cdot 3\text{NH}_3$, is obtained by gently warming a mixture of nickelous hydroxide, ammonia, and carbon bisulphide. It crystallises in transparent, ruby-red needles, is sparingly soluble in water, but easily in sodium hydroxide with an intense, yellowish-red coloration, and, when heated, gives off carbon bisulphide. On exposure to the air, it gives off part of the ammonia and carbon bisulphide.

The *iron salt*, $\text{Fe}_2\text{C}_2\text{S}_7 \cdot 6\text{NH}_3 + 2\text{H}_2\text{O}$, is obtained in a similar manner to the above. It crystallises in black, tetragonal prisms having a violet iridescence, and decomposes on exposure to air with glowing, and formation of ferric hydroxide. E. C. R.

Iron Nitrososulphides. By C. MARIE and R. MARQUIS (*Compt. rend.*, 1896, **122**, 137—140).—A quite neutral mixture of sodium nitrite, sodium sulphide, and ferrous sulphate, yields no iron nitrososulphide, even on boiling, but, on the addition of a small quantity of acid, the nitrososulphide is formed, and can be extracted with ether. With sufficient acid to decompose all the nitrite, however, the nitrososulphide is destroyed, and seems to be attacked in preference to the nitrite. The best acid to use is carbonic acid, and the best method is to suspend well washed ferrous sulphide in a solution of three times its weight of sodium nitrite, heat at 100° , and pass a current of carbonic anhydride through the liquid. The product forms black crystals of the composition $\text{Fe}_3\text{S}_2\text{N}_5\text{O}_6 + 1\frac{1}{2}\text{H}_2\text{O}$, and is soluble in water, alcohol, ether, chloroform, acetone, and ethylic acetate, but not in benzene or light petroleum. It alters when exposed to air, is decomposed by acids, and, when boiled with potassium hydroxide, yields ferric hydroxide, $\text{Fe}_2\text{O}_3(\text{OH})_2$, and a new nitrososulphide. When heated with water in sealed tubes at 220° , it yields ammonium sulphate, ferric oxide, and nitrogen, and, when heated alone at 200° , it yields ammonium thiosulphate, sulphite, and sulphate, and a green compound, which is under investigation. The nitrososulphide probably has the constitution, $\text{NO}_2 \cdot \text{Fe}[\text{S} \cdot \text{Fe}(\text{NO})_2]_2$. C. H. B.

Influence of Oxide of Iron and Alumina in the Reversion of Superphosphate. By ALFRED SMETHAM (*J. Soc. Chem. Ind.*, 1895, **14**, 112—114).—It has been customary of late years to stipulate in contracts concerning deliveries of raw phosphates, for a small minimum of oxide of iron and alumina, any excess to be considered as causing the reversion (precipitation) of double its weight of soluble phosphate.

The author has proved by a large number of experiments that, whereas this rule holds fairly good for the iron, it cannot be applied to the alumina, this substance only causing a reversion corresponding with its own weight. L. DE K.

Uranium Carbide. By HENRI MOISSAN (*Compt. rend.*, 1896, **122**, 274—280).—When 500 grams of green uranium oxide and 60 grams of sugar carbon are heated in the electric furnace with an arc from a current of 900 ampères and 50 volts for about 10 minutes, *uranium carbide*, C_3U_2 ($\text{U} = 240$) is obtained as a crystalline, lustrous solid, which scratches rock crystal, but not corundum; sp. gr. = 11.28 at 18° . When powdered, it begins to burn. Fluorine is without action in the cold, but the carbide burns in it when gently heated, and also in chlorine at 350° , oxygen or nitrogen peroxide at 370° , and bromine at 390° . Iodine attacks the carbide, without incandescence, below a red heat, and fused potassium nitrate or chlorate oxidises it with vivid incandescence. The carbide burns in sulphur

vapour at the melting point of glass, and in selenium at a lower temperature. Nitrogen attacks it at 1100° , but the conversion into nitride is incomplete. Dilute acids dissolve it slowly in the cold, and concentrated acids on heating. Hydrogen chloride and hydrogen sulphide attack it at about 600° , and ammonia partially converts it into a nitride at a red heat.

In contact with water, about one-third of the carbon is evolved in the form of a gaseous mixture containing acetylene, 0.2 to 0.7; ethylene, 5.0 to 7.0; methane, 78.0 to 81.0; and hydrogen, 13.5 to 15.0 per cent. by volume, whilst the remaining two-thirds of the carbon is converted into a mixture of liquid and solid hydrocarbons.

C. H. B.

Action of Nitric Peroxide on Stannic Salts. By V. THOMAS (*Compt. rend.*, 1896, **122**, 32—34).—When nitric peroxide is passed into a dilute solution of stannic chloride in chloroform, a white crystalline precipitate of the composition $\text{SnOCl}_2 \cdot 3\text{SnCl}_4 \cdot \text{N}_2\text{O}_5$ separates. It is hygroscopic and soluble in water, and, when heated, yields a white sublimate of the composition $3\text{SnCl}_4 \cdot 4\text{NOCl}$, identical with that described by Hampe.

Under similar conditions, stannic bromide yields a white compound, $\text{SnO}_2 \cdot 3\text{SnOBr}_2 \cdot \text{N}_2\text{O}_5$, which is partially decomposed both by water and by heat. Stannic iodide behaves differently; iodine is liberated, and the white compound that is formed has the composition $\text{Sn}_5\text{O}_{11}(\text{NO}_3)_2 + 4\text{H}_2\text{O}$, and, is, therefore, analogous to the alkali metastannates, except that the alkali metal has been replaced by the group NO_3 .

C. H. B.

Tin Thiophosphide. By A. GRANGER (*Compt. rend.*, 1896, **122**, 322—323).—When phosphorus and stannic sulphide are heated below the softening point of glass in adjacent dishes in a glass tube, and the vapour of the former is carried over the latter by means of a current of carbonic anhydride, a *tin thiophosphide*, $\text{Sn}_2\text{P}_2\text{S}$ or $\text{SnP} \cdot 2\text{NS}$, is obtained in brilliant, grey-black scales. It is oxidised when heated in air, and yields stannic and phosphoric anhydrides, but is not attacked by nitric or hydrochloric acid or by aqua regia. Chlorine and bromine attack it in the cold, and, when finely powdered, it dissolves in solutions of alkali hydroxides through which chlorine or bromine vapour is passed.

C. H. B.

Alums of Titanium Sesquioxide. By AUGUSTO PICCINI (*Gazzetta*, 1895, **25**, ii, 542—543).—On dissolving titanic hydrate in dilute sulphuric acid, adding the proper quantity of caesium sulphate, and electrolysing the liquid, it assumes a deep violet colour, and deposits *caesium titanium alum*, $\text{Cs}_2\text{SO}_4 \cdot \text{Ti}_2(\text{SO}_4)_3 + 24\text{H}_2\text{O}$; this consists of cubic crystals showing pyramidal hemihedrism, and has a violet colour, but less intense than that of the corresponding vanadium alum. It rapidly changes in the air, turning white and deliquescent; when heated it loses water and sulphuric acid. It is very sparingly soluble in cold water, and is decomposed by hot water with separation of titanic acid.

W. J. P.

Mineralogical Chemistry.

Examination of Terrestrial Emanations for Argon. Gas from Thermæ of Abano. By RAFFAELE NASINI and FRANCESCO ANDERLINI (*Gazzetta*, 1895, **25**, ii, 508—509).—Some 2000 to 3000 litres of gas issue per hour from the central hot spring of Monte Irone, in Abano, recently analysed by the authors (Abstr., 1894, ii, 422). The gas does not contain argon, but consists of the following percentages of various gases: 1.13 of H_2S , 10.73 of CO_2 , 0.40 of O_2 , 75.74 of N_2 , and 12.00 of methane mixed with small quantities of other organic substances. W. J. P.

Graphitoid. By WILLI LUZI (*Zeit. Kryst. Min.*, 1896, **25**, 611; from *Berg- und Hüttenm. Zeit.*, 1893, **52**, 11—13).—Two analyses of graphitoid, which was isolated by means of acids from the quartzschist of Kleinolbersdorf, Saxony, gave, after deducting 15.34 and 2.48 per cent. of ash, C = 99.02 and 98.82, H = 0.54 and 0.30 per cent. respectively. Oxygen is also present. From this composition, it is considered that graphitoid, which burns at a fairly low temperature, is not a modification of carbon. L. J. S.

Sperrylite. By T. L. WALKER (*Zeit. Kryst. Min.*, 1896, **25**, 561—564; and *Amer. J. Sci.*, 1896, [4], **1**, 110—112).—The crystals from the only locality known for this mineral (namely Vermilion mine, Algoma District, Ontario), are described, the forms (111), (001), $\pi(210)$, and $\pi(10.5.2)$ being present; the crystals are embedded in copper pyrites, but not in the associated pyrrhotite. Sperrylite is dissolved by aqua regia, and more slowly by hydrochloric acid, but is almost insoluble in nitric, sulphuric, and hydrofluoric acids. It is suggested that the metals of the platinum group found in the copper-nickel ores of this district may occur as replacing platinum in sperrylite. An analysis is given of a copper-nickel matt, showing small quantities of gold, silver, platinum, iridium, osmium, and traces of rhodium and palladium. L. J. S.

Etching of Calcite. By AXEL HAMBERG (*Jahrb. Min.*, 1896, i, Ref. 216—222; from *Geol. För. Förh.*, 1895, **17**, 53—73, 453—472).—Plates of Iceland spar were cut in various definite directions, and the loss of weight per unit area (or sometimes the reduction in thickness) determined after they had been allowed to remain in hydrochloric acid. The solubility coefficient for any particular face at any definite temperature, is defined as the amount of calcite in grams dissolved from 1 sq. cm. in one second by hydrochloric acid of sp. gr. 1.09. If l_t be this coefficient at t° , then, at T° it is $l_T = l_t (1.07473)^{(T-t)}$.

The results obtained are the more accurate when dissolution takes place more quickly. On the easily soluble faces, solution proceeds regularly without the formation of etch figures; but on (100) and

(111) etch figures are developed, dissolution having here gone on in the direction of other planes. Confirmatory results were obtained with calcite cylinders cut in various zones.

Face.	Coefficient at 0·4°.	Coefficient at 15°.	Coefficient at (about) 30°.	
OR (111).....	0·000201	0·000551	0·00167	0·69
∞R (2II).....	0·000130	0·000335	0·00115	1·02
∞P2 (0II).....	0·000125	0·000278	0·00093	1·00
-2R (1II).....	0·000064	0·000149	0·00061	0·67
+ R (100).....	0·000054	0·000159	0·00072	0·94
+ 4R (3II).....	0·000140	0·000523	0·00153	—
-½R (101).....	0·000213	0·000580	0·00164	0·78
+ R2 (30I).....	0·000237	0·000670	0·00179	—
+ 2R (5II).....	0·000236	0·000726	0·00197	1·17

With more dilute acid, the same maxima and minima occur, but the difference between them is less. Numerous measurements are given, showing the effects of the presence of calcium chloride and sugar (a non-dissociable substance) with the hydrochloric acid. Acetic acid was also used. The last column in the above table gives the relative solubilities when water containing carbonic anhydride under a pressure of 6 atmos. is used; here sharp etch figures are developed on the basal plane.

L. J. S.

Thaumasite from West Paterson, New Jersey. By SAMUEL L. PENFIELD and JULIUS H. PRATT (*Amer. J. Sci.*, 1896, [4], 1, 229—233). This mineral, of anomalous composition, has previously only been found in Sweden; it is now described from West Paterson, N. J., where it occurs in considerable quantity with zeolites in a trap rock. It consists of an aggregation of prismatic crystals, sometimes loose, but more often firm, and resembling white alabaster in appearance. There is a distinct prismatic cleavage, and prism angles of about 60°. The mineral is optically uniaxial and negative; $\omega = 1·519$ (another determination 1·5125), $\epsilon = 1·476$ approx. The sp. gr. is between 1·887 and 1·875; analysis gave

SiO ₂ .	CO ₂ .	SO ₃ .	CaO.	H ₂ O.	Na ₂ O.	K ₂ O.	Total.
9·26	6·82	13·44	27·13	42·77	0·39	0·18	99·99

This agrees with the usual formula, $\text{CaSiO}_3, \text{CaCO}_3, \text{CaSO}_4, 15\text{H}_2\text{O}$. The alkalis exist as impurities, as is shown by their being dissolved, together with a very little thaumasite, in water. For the loss of water, constant weights are obtained at the temperatures 150°, 200°, 250°, 300°, and below redness, the loss in each case being 37·41, 1·82, 1·41, 1·05, 1·08 = 42·77 per cent., respectively. The 13 mols. of water lost up to 150° are considered as water of crystallisation, whilst the four other portions, which are given off at different temperatures, represent four hydroxyl groups which play different parts in the con-

stitution of the mineral. The results are considered to render probable the structural formula $\text{OH}\cdot\text{Si}(\text{O}\cdot\text{CO}\cdot\text{Ca}\cdot\text{OH})_2\cdot\text{O}\cdot\text{Ca}\cdot\text{OH} + 13\text{H}_2\text{O}$.

L. J. S.

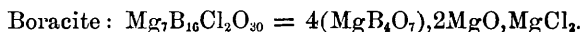
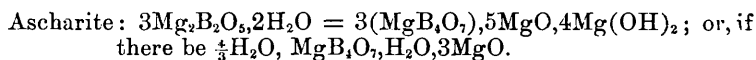
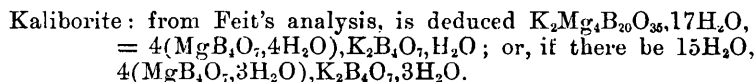
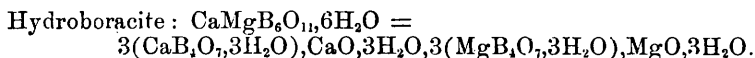
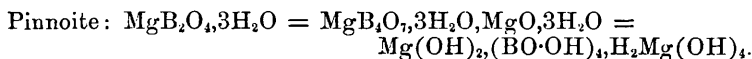
Salvadorite, a new Copper Iron Sulphate. By WALTER HERZ (*Zeit. Kryst. Min.*, 1896, **26**, 16—18).—This was found as an aggregate of bluish-green and blue crystals, cemented together by weathered iron sulphate, in the Salvador mine, Quetena, Calama, Chili. The somewhat indistinct and rounded crystals are monosymmetric, with $b(010)$, and a prism with an angle of $48^\circ 16'$ in front. The plane of symmetry is the direction of perfect cleavage, and is the plane of the optic axes. The extinction to the vertical axis is 52° for Na and $46\frac{1}{2}^\circ$ for Tl light; optic axial angle 76° for Na and 87° for Tl light. Analysis of crystals gave

	FeO.	CuO.	SO ₃ .	H ₂ O.	Total.
I (green)	8.49	18.77	27.87	44.65	99.78
II (blue)	9.59	17.57	28.16	44.31	99.63

Formula, $\text{FeCu}_2(\text{SO}_4)_3 + 21\text{H}_2\text{O}$. Salvadorite thus resembles pisanite in composition and crystalline system, but differs in the crystal habit and angle, in the cleavage, and in the angle of optical extinction. The two minerals may be dimorphous, or one may be an isomorphous mixture and the other a molecular compound, perhaps in salvadorite as $(\text{FeSO}_4, 7\text{H}_2\text{O}), 2(\text{CuSO}_4, 7\text{H}_2\text{O})$.

L. J. S.

Borates in the Stassfurt Abraum Salts. By H. BERNHARD KOSMANN (*Zeit. deutsch. geol. Ges.*, 1893, **45**, 167—170).—For the borates occurring in the abraum salts of the Stassfurt district, the following formulæ are written.



L. J. S.

Action of Sulphuric and Hydrochloric acids on Heulandite: an artificial form of Silica. By FRIEDRICH RINNE (*Jahrb. Min.*, 1896, i, 139—148).—When heulandite ($\text{CaAl}_2\text{Si}_6\text{O}_{16} + 4\text{H}_2\text{O}$) is placed in anhydrous sulphuric acid, the effect is the same as when the mineral is heated at 150° ; there being a loss of $2\text{H}_2\text{O}$, and a change in the optical characters; for example, the optic axes pass twice through a uniaxial position until their plane is $b(010)$, the extinctions in the new position conforming with orthorhombic symmetry. When

placed in water, there is a change back again to the characters of heulandite.

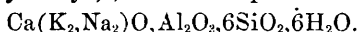
Dilute sulphuric acid, or hydrochloric acid, completely decomposes the mineral, leaving silica having the form of the heulandite cleavage flakes; this silica shows a negative bisectrix perpendicular to the plate, the magnitude of the optic axial angle varying in different fields; the double refraction is fairly strong. When heated to redness, there is a loss of about 8·8 per cent. of water, but no change in the optical characters. The sp. gr. of 2·143 is near to that of tridymite and of cristobalite, but the optical characters differ.

L. J. S.

Desmine [Stilbite] and Laumontite from the Caucasus. By PETR. A. ZEMJATSCHENSKY (*Zeit. Kryst. Min.*, 1896, **25**, 574; from *Rev. sci. natur.*, 1893, 335—344).—The optical anomalies of stilbite (from Mt. Borschom, near Tiflis) are explained by the nearly parallel aggregation of small crystal individuals. White, radially fibrous laumontite from the same locality gave analysis I; from this is deduced the formula $\text{Ca}(\text{K}_2)\text{O}, \text{Al}_2\text{O}_3, 4\text{SiO}_2, 4\text{H}_2\text{O}$.

	SiO_2 .	Al_2O_3 .	CaO .	MgO .	K_2O .	Na_2O .	H_2O (over H_2SO_4).
I.	52·45	22·05	10·15	0·52	1·40	Nil.	—
II.	57·77	15·76	7·35	Nil.	1·14	0·63	1·98
	H_2O (at 100°).		H_2O (on ignition).		Total.		
I.	2·01		14·18		102·76		
II.	—		17·28		99·93		

Platy and radially fibrous, pale rose-coloured stilbite, from Surám, gave analysis II (by Malys); this corresponds with



L. J. S.

Fluorine in Apophyllite. By ADOLF E. NORDENSKIÖLD (*Zeit. Kryst. Min.*, 1896, **26**, 92; from *Geol. För. Förh.*, 1894, **16**, 579).—Friedel has failed to find fluorine in the apophyllite of Bou Serdoun, Utö, and Andreasberg (Abstr., 1894, ii, 421). It is pointed out that Berzelius, in 1822, etched glass with the hydrofluoric acid obtained by the action of sulphuric acid on the calcium fluoride derived from apophyllite; and the author obtains the same result with the apophyllite of Utö, Nordmark, Hellestad, Poona, and Bou Serdoun (compare Abstr., 1895, ii, 276; this vol., ii, 114; also *Zeit. Kryst. Min.*, **26**, 221). The presence of ammonium chloride in the mineral observed by Friedel was noticed by V. Rose in 1805 (*Gehlen's Journal*, 1805, **5**, 35).

L. J. S.

Clarke and Schneider's Constitutional Formula for Serpentine. By A. LINDER (*Zeit. Kryst. Min.*, 1896, **25**, 589—592; from *Inaug. Diss.*, Breslau, 1893, 1—36).—From the action of dry hydrogen chloride on serpentine, Clarke and Schneider deduced the formula $\text{Mg}_2(\text{SiO}_4)_2\text{H}_3(\text{MgOH})$, only the group $-\text{Mg}\cdot\text{OH}$ being supposed to be acted on by the gas (Abstr., 1891, i, 529). The author repeats these experiments, using 19 serpentines of different texture, &c., and from

various localities, and finds that no constant amount of magnesium chloride (such as would correspond with $\text{Mg}\cdot\text{OH}$ in the above formula) is formed by the action of the dry gas at about 400° , and also at $130\text{--}150^\circ$; thus at 400° the ratio of the amount of MgCl_2 formed to the original amount of MgO varies from $5\cdot3 : 100$ to $66\cdot7 : 100$. The ferrous iron was also attacked by the gas, but usually to a less extent than the magnesium. Experiments were also made, using as reagents, bromine, ammonium chloride, dry and in solution, acetic acid, potassium and sodium hydroxides, but varying results were obtained. Complete analyses of the 19 serpentine used are given.

L. J. S.

Lawsonite, a new Rock-forming Mineral from California.

By F. LESLIE RANSOME and CHARLES PALACHE (*Bull. Dept. Geol. Univ., California*, 1895, **1**, 301—312; and *Zeit. Kryst. Min.*, 1896, **25**, 531—537).—Lawsonite occurs as a rock-forming mineral in a crystalline schist at the Tiburon Peninsula, Marion Co., California, in large, tabular crystals embedded in margarite veins, and also in crystals of octahedral or prismatic habit lining and filling cavities. The crystals are orthorhombic, with few forms, and are often twinned on the prism plane; $a : b : c = 0\cdot6652 : 1 : 0\cdot7385$; cleavage $b(010)$ perfect, $c(001)$ less perfect, $m(110)$ indistinct. The small crystals, when fresh, are clear and colourless, but the larger are of a greyish-blue colour of unequal distribution, much resembling kyanite. The plane of the optic axes is $b(010)$, the acute bisectrix being perpendicular to $c(001)$, optically positive; for sodium light, $2V = 84^\circ 6'$, $\alpha = 1\cdot6650$, $\beta = 1\cdot6690$, $\gamma = 1\cdot6840$; strongly pleochroic in the coloured portions. Hardness about 8, brittle; sp.gr. $3\cdot084$ (in powder $3\cdot091$). Easily fusible. The mineral is only slightly acted on by boiling, strong hydrochloric acid, but is completely decomposed by hydrochloric acid in a sealed tube at 140° . Analysis gave

SiO_2 .	Al_2O_3 .	Fe_2O_3 .	CaO .	MgO .	Na_2O .	H_2O .	Total.
38·10	28·88	0·85	18·26	0·23	0·65	11·42	98·39

At 225° there is a loss of only $0\cdot1$ per cent. Formula, $\text{H}_4\text{CaAl}_2\text{Si}_2\text{O}_{10}$, or as a basic meta-silicate, $2\text{Al}(\text{OH})_2\cdot\text{Ca}(\text{SiO}_3)_2$; this is similar to carpholite, $\text{H}_4\text{MnAl}_2\text{Si}_2\text{O}_{10}$ (monosymmetric?), with which lawsonite is probably isomorphous, the prism angles of the two minerals being nearly equal. The associated minerals of the schist are margarite, epidote, actinolite, glaucophane, and red garnet.

L. J. S.

Minerals (Zeolites, &c.) of a Thuringian Amphibole-granite. By JOHANNES FROMME (*Zeit. Kryst. Min.*, 1896, **25**, 616—617; from *Sitzb. phys.-med. Soc., Erlangen*, 1893, **25**, 26—53).—The rock is from near Suhl; from it orthoclase, oligoclase, and lepidomelane were isolated, and in the cavities occur calcite, epidote, hematite, pyrites, stilbite, scolecite, chabazite, and heulandite. The results of the analyses are given under I for the reddish orthoclase, II, white oligoclase, somewhat decomposed, and mixed with orthoclase; after deducting orthoclase, the composition is Ab_3An ; III, lepidomelane, in very thin plates, brown-yellow, and transparent; IV, stilbite, brownish

or yellowish aggregates; V, scolecite, white, radially fibrous aggregates; VI, chabazite, reddish-yellow, mostly simple rhombohedra; VII, heulandite, in good crystals.

	I.	II.	III.	IV.	V.	VI.	VII.
SiO ₂ ...	63.19	61.52	34.14	56.42	45.75	50.62	58.31
Al ₂ O ₃ ...	19.48	24.31	17.78	16.11	26.54	17.14	16.69
Fe ₂ O ₃ ..	0.38	0.48	5.78	0.19	trace	0.42	trace
FeO....	—	—	13.59	—	—	—	—
MnO... ..	—	—	1.59	—	—	—	—
CaO ...	0.59	4.14	2.07	8.31	13.16	8.77	8.84
SrO....	—	—	—	—	—	trace	
MgO ...	trace	trace	13.21	—	—	—	—
K ₂ O ...	11.59	2.32	5.70	0.78	trace	1.15	0.79
Na ₂ O... ..	4.20	6.10	1.16	0.23	0.59	0.79	0.35
H ₂ O ...	0.51	1.65	4.50	17.77	13.75	20.74	15.62
	99.94	100.52	99.52	99.81	99.79	99.63	100.60
Sp. gr...	2.564	2.666	3.015	2.168	2.272	2.09	—

As the zeolites have been derived from the feldspars, the latter were tested for strontium, but with negative result. The calcite is generally of earlier date than the scolecite, but later than the other zeolites.
L. J. S.

Gehlenite and Wollastonite in Slags from Příbram. By PH. HEBERDEY (*Zeit. Kryst. Min.*, 1896, **26**, 19—27).—The slags described are produced on smelting the impure fahl ore of Příbram. On the black, cryptocrystalline ground-mass are tabular crystals of gehlenite and columnar crystals of wollastonite; the latter, which gave crystallographic measurements, being of rare occurrence in slags as crystals of any size. Thin sections of the ground mass showed a few crystals of gehlenite, and numerous colourless needles of wollastonite and of the hexagonal calcium silicate. The ground-mass is nearly all decomposed by hydrochloric acid; from its analysis is deduced $50\text{CaSiO}_3 + 18\text{FeSiO}_3 + 4\text{Fe}_2\text{SiO}_4 + 6\text{MgO} \cdot \text{Al}_2\text{O}_3 + 11\text{FeS} + 7\text{ZnS} + 9\text{MnS} + \text{PbS}$. The calcium metasilicate exists as wollastonite, and in the hexagonal form, but it is doubtful how the FeSiO_3 occurs.
L. J. S.

Epidote from Huntington, Mass.; and the Optical Properties of Epidote. By E. H. FORBES (*Amer. J. Sci.*, 1896, [4], **1**, 26—30; and *Zeit. Kryst. Min.*, 1896, **26**, 138—142).—In the gneiss of Huntington, Mass., are transparent, dark grey crystals of epidote; analysis gave

SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	FeO.	MnO.	CaO.	H ₂ O.	Total.	Sp. gr.
37.99	29.53	5.67	0.53	0.21	23.85	2.04	99.82	3.367

This gives the usual formula; the iron is low for epidote.

Crystallographic determinations are given. The extinction angle, $\alpha : c$ is $1^\circ 51'$ Li, $2^\circ 9'$ Na, $2^\circ 12'$ Tl, in the obtuse angle β ; $2V_{\text{Na}} = 89^\circ 28'$, $\rho < v$, optically positive (other epidotes are negative with $\rho > v$). The green portion of a pink and green zoned crystal from

the Zillerthal gave Fe_2O_3 6.97, FeO 0.89 per cent.; the inner green portion gave the extinction angle $\alpha : c = 0^\circ 30'$, in the acute angle β , and the outer pink portion gave $0^\circ 30'$ in the obtuse angle β , for white light. The determinations for sodium light are compared with those of Klein (1874) for the Untersulzbachthal crystals, showing a gradual change in the magnitude of the optical constants with the amount of iron.

	Fe_2O_3 .	α .	β .	γ .	$\gamma - \alpha$.	2V over α .
(Klein)....	14.0	1.7305	1.7540	1.7677(r)	0.0372	$73^\circ 39'$
Zillerthal..	6.97	1.720	1.7245	1.7344	0.0144	87 46
Huntington	5.67	1.714	1.716	1.724	0.010	90 32

L. J. S.

Minerals of the Nepheline-syenite of Greenland. By N. V. USSING (*Zeit. Kryst. Min.*, 1896, **26**, 104—107; from *Meddelelser om Grønland*, 1893-4, **14**).—The principal rock-forming minerals of the nepheline-syenite of S. Greenland are described; these being feldspars, nepheline, sodalite, eudialyte, amphiboles, and pyroxenes; lime feldspars are absent. The following analyses, by C. Detlefsen, of the alkali-feldspars are given: I, microcline from Kunerngit; II, microcline-micropertthite from Serrarsuit, after deducting 1.56 per cent. of enclosed ægyrite; III, cryptoperthite from Narsasik.

	SiO_2 .	Al_2O_3 .	Fe_2O_3 .	MgO .	Na_2O .	K_2O .	Loss on ignition.	Total.	Sp. gr.
I. 64.68	19.04	0.24	trace	0.53	15.82	—	—	100.31	2.567
II. 65.86	18.76	—	—	3.34	12.04	—	—	100.00	2.580
III. 65.81	19.43	0.40	—	5.61	8.66	0.39	—	100.30	—

The arfvedsonite is often altered into acmite; the following analysis of the altered material, showing that the change consists mainly in the oxidation of the ferrous oxide (33.43 per cent. of which is given in Lorenzen's analysis of arfvedsonite from this locality).

SiO_2 .	Al_2O_3 .	Fe_2O_3 .	FeO .	MnO .	MgO .	CaO .	K_2O .
44.19	4.63	34.67	1.16	0.45	0.18	2.35	0.13
		Na_2O .	H_2O .	Total.	Sp. gr.		
		11.61	0.30	99.67	3.571		

L. J. S.

The Olivine Group. By KONSTANTIN THADDÉEFFF (*Zeit. Kryst. Min.*, 1896, **26**, 28—78).—With the view of tracing a connection between the chemical composition and the sp. gr. of the members of the olivine group, analyses have been made of the Vesuvian forsterite (this vol., ii, 309), the olivine of Dreiser Weiher in the Eifel, I, and of the olivine of Skurruvaselv in Norway, II.

	SiO_2 .	FeO .	MgO .	NiO .	MnO .	Al_2O_3 .	H_2O .	Total.	Sp. gr.
I. 40.99	8.37	50.00	0.37	0.14	0.40	—	—	100.27	3.335
II. 38.59	20.29	39.78	—	0.32	0.86	0.40	—	100.24	3.497

These, as well as numerous quoted analyses, show that the FeO and the sp. gr. increase together. From his determinations of FeO and the sp. gr., the author, assuming an isomorphous series, calculates

the sp. gr. of the extreme members of the olivine group, namely Mg_2SiO_4 and Fe_2SiO_4 , to be 3.198, and 4.745, respectively. The specific gravities calculated from these values agree with those observed for forsterite and olivines, but in the case of hortonolite and fayalite (observed about 4.35) there are considerable deviations. It is, therefore, considered that in olivine the Fe_2SiO_4 is of a denser modification than in fayalite, and that the whole group forms two independent isomorphous series, similar to those shown by mixed salts of $\text{FeSO}_4 + 7\text{H}_2\text{O}$, and $\text{MgSO}_4 + 7\text{H}_2\text{O}$, as described by Rammelsberg and Retgers; the interval in this case, in which mixed salts do not occur, being, perhaps, between hyalosiderite and hortonolite; for the sp. gr. of the Mg_2SiO_4 in the members at the iron end of the group is calculated 3.278, this being near to that of Ebelmen's artificial forsterite. A similar relation exists in the case of the crystallographic constants as pointed out by Bauer; the a and c axes increasing slightly in magnitude with the iron as far as hyalosiderite, whilst for fayalite they again decrease.

In analysis II, the water was determined by ignition in dry hydrogen freed from oxygen; determinations were made to find the amount of ferrous iron oxidised when olivine is ignited in the presence of air.

L. J. S.

Fayalite from Rockport, Mass.; and the Optical Characters of the Olivine Group. By SAMUEL L. PENFIELD and E. H. FORBES (*Amer. J. Sci.*, 1896, [4], 1, 129—135; and *Zeit. Kryst. Min.*, 1896, 26, 143—149).—Dark green, massive fayalite, associated with magnetite in the granite of Rockport, Mass., gave analysis I (mean of two); the water is considered to be basic, as it is only expelled at a high temperature, and when calculated with RO the ratio $\text{SiO}_2:\text{RO} = 0.501:1.004$. The optical constants are given under A.

Hortonolite from Monroe, New York, gave analysis II (mean of two), and optical constants B.

Monticellite from Magnet Cove, Arkansas, gave analysis III (mean of two); the water is here neglected as being due to decomposition; optical constants C.

	SiO_2 .	FeO .	MnO .	MgO .	CaO .	H_2O .	Total.	Sp. gr.
I.	30.08	68.12	0.72	nil	—	0.80	99.80	4.318
II.	33.77	47.26	4.54	13.88	—	0.48	99.93	4.038
III.	36.78	4.75	1.62	21.60	34.31	0.95	100.01	3.035
	α_{Na} .	β_{Na} .	γ_{Na} .	V_{Na} .	$2H_{\text{Li}}$.	$2H_{\text{Na}}$.	$2H_{\text{Ti}}$.	
A.	1.8236	1.8642	1.8736	$24^\circ 55'$	$57^\circ 27'$	$56^\circ 32'$	$55^\circ 2'$	
B.	1.7684	1.7915	1.8031	$34^\circ 42'$	$76^\circ 59'$	$76^\circ 0'$	$75^\circ 45'$	
C.	1.6505	1.6616	1.6679	$37^\circ 31'$	$75^\circ 55'$	$75^\circ 21'$	$74^\circ 52'$	

The following table shows that in the olivine group (excluding monticellite) as the amount of iron decreases there is a gradual increase in the value of the optic axial angle, the latter changing less rapidly at the magnesium end of the series; the value of β and the strength of double refraction decrease with the iron.

	FeO per cent.	2V _{Na} over α .	β_{Na} .
Fayalite, Rockport.....	68.1	49° 50'	1.864
Hortonolite, Monroe	47.3	69 24	1.791
Olivine, Auvergne.....	13.0	89 36	1.692
„ Vesuvius	12.6	89 42	—
„ Hawaii	10.3	91 2	—
„ Egypt.....	9.2	91 19	1.678
„ New Mexico.....	8.6	91 24	—
Forsterite, Vesuvius (Des Cloiseaux)	2 ?	93 50	1.657

In the olivine group we always have $a = c$, $b = a$, $c = b$, but when there is less than about 12 per cent. of FeO, the acute bisectrix is c (except in monticellite), and with more iron it is a ; in the former case the mineral is optically positive with $\rho < v$, and in the latter negative with $\rho > v$.
L. J. S.

A new Alkali Hornblende and a Titaniferous Andradite from Dungannon, Ontario. By FRANK D. ADAMS and BERNARD J. HARRINGTON (*Amer. J. Sci.*, 1896, [4], 1, 210—218).—In the nepheline-syenite of Dungannon, Hastings Co., Ontario (Abstr., 1894, ii, 461), two varieties of hornblende occur in different parts of the mass; one of these is near to common green hornblende, although it contains a considerable amount of soda; the other is quite different. It has a small optic axial angle (30° or 45°), a large extinction angle ($c : c = 30^\circ$), low double refraction, and pleochroism a yellowish-green, b and c deep bluish-green. Analysis I; calculating the titanium with the silicon, this gives the orthosilicate formula $(R'_2, R'')_3 R_2'' Si_3 O_{12}$; this is the same as that given by Scharizer for “syntagmatite” in his theory of the composition of aluminous amphiboles (Abstr., 1885, 32). No other hornblende analysis shows so little silica as this. Hornblendes with similar optical characters occur at Montreal and at Umptek in the Kola Peninsula.

	SiO ₂ .	TiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	FeO.	MnO.	CaO.	MgO.
I.	34.184	1.527	11.517	12.621	21.979	0.629	9.867	1.353
II.	36.604	1.078	9.771	15.996	3.852	1.301	29.306	1.384

	K ₂ O.	Na ₂ O.	Loss on ignition.	Total.	Sp. gr.
I.	2.286	3.290	0.348	99.601	3.433
II.	—	—	0.285	99.577	3.739

A brown, isotropic garnet occurs as irregular grains in the same nepheline-syenite; it encloses calcite (apparently not secondary) hornblende, pyrites, iron ore, and nepheline. Analysis II; calculating the titanium as Ti₂O₃, the garnet formula is deduced. Similar garnets occur at Montreal, Stokö, and Alnö.
L. J. S.

Chemical Behaviour of some naturally occurring Titanium Compounds. By RUDOLF SOLTSMANN (*Zeit. Kryst. Min.*, 1896, 25, 617—618; from *Inaug. Diss.*, Bern, 1893).—The follow-

ing analyses of sphene were made with the view of ascertaining whether in the light coloured, especially green, specimens the ratio Si:Ti = 1:1 holds.

I. Yellow-green plates, (001), from Rothenkopf, Zillertal, Tyrol.

II. Twins in chlorite from Trümmelbachthal, Prägeraten.

III. Light reddish-yellow or pale-greenish crystals in pebbles of hornblende-gneiss, near Meran.

	SiO ₂ .	TiO ₂ .	CaO.	FeO.	MnO.	H ₂ O.
I.	31.53	35.48	28.35	1.89	—	0.36
II.	33.05	37.10	29.79	—	—	0.36
III.	33.38	38.51	29.73	—	trace	—

The single analyses, of which the above are the means, showed fairly wide variations, so that a deviation from the normal ratio could not be deduced.

L. J. S.

Meteorite from Forsyth Co., North Carolina. By EMILE A. DE SCHWEINITZ (*Amer. J. Sci.*, 1896, **1**, [4], 208—209).—A mass weighing about 50 lbs. was ploughed up about three years ago in the south-west portion of Forsyth Co. No characteristic etching was produced on polished surfaces; preliminary analysis gave

Fe.	S.	Ni.	Co.	P.
94.90	0.22	4.18	0.33	trace

From this it would seem to be closely allied to the Guilford Co. meteorite, possibly a chip of the same find.

L. J. S.

Physiological Chemistry.

Digestibility of the Pentosans of Vegetable Foods. By HUGO WEISKE (*Bied. Centr.*, 1896, **25**, 13—15; from *Oesterr. Ung. Zeits.*, 1895, No. 24, 594).—Two sheep were fed on meadow hay (706.72 grams of dry substance) and oats (219 grams of dry substance), containing respectively 27.64 and 15.55 per cent. of pentosans respectively. Determinations of the pentosans in the fæces of the sheep during the three periods of the experiment showed that an average of 65.1 per cent. was digested. In experiments with rabbits fed on oats, 53.81 per cent. of the pentosans was digested. Assuming the digestive powers of sheep and rabbits to be the same, the pentosans of oats seem to be less digestible than those of meadow hay.

The question whether the pentosans which are digested have a food value remains to be decided (compare Abstr., 1895, ii, 278).

N. H. J. M.

Partition of Urea between Blood Corpuscles and Blood Serum. By BERNHARD SCHÖNDORFF (*Pflüger's Archiv*, 1896, **63**,

192—202).—Urea is a constituent of red blood corpuscles; the amount of urea in the blood is equally divided between corpuscles and serum. If an isotonic solution of urea is added to the blood, the urea is equally shared by the corpuscles and serum. If an isotonic solution of sodium chloride is added, the urea leaves the corpuscles until there is an equal amount in the diluted serum. W. D. H.

Osmotic Pressure of Blood-plasma, and the Formation of Hydrochloric acid in the Stomach. By HANS KOEPPE (*Pflüger's Archiv*, 1896, **62**, 567—602).—Inorganic salts increase the energy of the organism; this is seen in the phenomena of diffusion and the action of osmotic pressure.

The action of salt solutions on the osmotic pressure can be estimated by the hæmatocrite; this is especially applicable to blood-plasma. The osmotic pressure of blood-plasma undergoes by no means unimportant variations, being always increased by the midday meal; this is the result of the secretion of hydrochloric acid in the stomach.

In order to equalise the difference between the osmotic pressure of the blood-plasma and that of the stomach contents (that is, a strong solution of sodium chloride) as rapidly as possible, a flow of water into the stomach and a passage of salt into the blood occurs; the stomach wall is impermeable for free chlorine ions, but the sodium ions of the sodium chloride are exchanged for the hydrogen ions of the blood. In the stomach, free chlorine and hydrogen ions are found, hence its contents give the reactions for hydrochloric acid; the acid of the stomach is formed in the stomach wall, the stimulus for its separation being free chlorine ions in the stomach. This explanation of the formation of hydrochloric acid out of the chlorides of the stomach contents depends on the presence of free hydrogen ions in the blood. This is the case, for (a) water contains free hydrogen and free hydroxyl ions; (b) in the blood, free carbonic anhydride and primary carbonates and phosphates are present. From these materials the hydrogen ion is one of the dissociation products. (c) After the exit of the few hydrogen ions from the blood, more are formed by further dissociation.

This explanation of the formation of the hydrochloric acid of the stomach stands in complete accord with the following experimental premisses. (a) In spite of the formation of an acid, the cell remains alkaline; (b) the alkalinity of the blood is increased; (c) in the absence of free chlorine ions in the stomach contents no hydrochloric acid is formed; (d) injection of hydrochloric acid into a vein causes no appearance of that acid in the stomach; (e) the formation of other acids (hydrobromic, hydriodic) follows the introduction of the sodium salts of the corresponding halogens into the stomach; (f) after taking much sodium chloride, the urine may become alkaline.

W. D. H.

Fat Absorption. By ISAAC LEVIN (*Pflüger's Archiv*, 1896, **63**, 171—191).—The absorption of fat from the alimentary canal takes place in two ways, (1) in the form of soluble soaps, (2) in the form of fat droplets. For the latter to occur, not only is emulsification

necessary, but the presence of both bile and pancreatic juice is essential for the purpose of stimulating the epithelial cells to take up the fat. If either, or both, are absent, even though emulsification occurs, the chyle is free from fat. The fat droplets are taken up as such, not synthesised within the cells. W. D. H.

Influence of Muscular Work on Proteid Metabolism. By OTTO KRUMMACHER (*Zeit. Biol.*, 1896, **33**, 108—138).—This research (three experiments) performed on human beings was carried out under Voit's supervision. It is pointed out that Voit never denied that proteid metabolism was increased by muscular work; he stated that the chief source of the energy was not proteid. Pflüger and his pupils did their work on an insufficient diet, and so more proteid in the muscle would have to be used up as a source of energy than is usually the case. The present experiments show a small increase in the excretion of nitrogen during rest as compared with work. Full details of ingesta and excreta and the work done (turning the handle of a dynamometer) are given. W. D. H.

Mineral Constituents of Flesh. JULIUS KATZ (*Pflüger's Archiv*, 1896, **63**, 1—85).—The flesh of a large number of animals was investigated, and the results are given in detail. The following numbers give the minimum and maximum in 1000 parts of fresh flesh. K, 2·4 to 4·6; Na, 0·3 to 1·5; Fe, 0·04 to 0·25; Ca, 0·02 to 0·39; Mg, 0·18 to 0·37; P, from phosphates, 1·22 to 2·04, from lecithin, 0·13 to 0·48, from nuclein, 0·09 to 0·32; Cl, 0·32 to 0·8. W. D. H.

Action of Related Chemical Substances on Striped Muscle. By ARTHUR BLUMENTHAL (*Pflüger's Archiv*, 1896, **62**, 513—542).—In order to make comparative experiments with various chemical materials on living tissues, it is necessary to employ solutions of equal molecular strengths.

Decinormal solutions of the sodium compounds of the halogens stimulate and then destroy muscle; sodium iodide is the most, and sodium chloride the least, powerful. Sodium fluoride is more powerful than the iodide.

The chlorides of potassium, rubidium, and caesium act as stimulants and then destroy muscle; their activity as stimulants varies with their molecular weights, and as paralyzers in the reverse direction. The action of the chlorides of calcium, strontium, and barium is precisely analogous.

With the alkalis (centinormal solutions), the rise of excitability is small; ammonia is most destructive, then potassium hydroxide, then sodium hydroxide.

The inorganic acids (1/200 normal) are destructive in proportion to their avidity, hydrochloric and nitric acids being about equal, then sulphuric acid and, lastly, phosphoric acid.

As regards power of destruction, the fatty acids stand in the order of their molecular weights; the only exception being formic acid, which is more injurious than acetic acid.

The alcohols have a similar relationship; here again, however, methylic alcohol is more poisonous than ethylic alcohol.

Fick's view of muscular activity, that the two processes of shortening and lengthening are independent and separate vital processes, is supported by the fact that some reagents affect only the one and others only the other phase.

W. D. H.

Chemistry of some Marine Animals. By EDMUND DRECHSEL (*Zeit. Biol.*, 1896, **33**, 85—107).—The fresh liver of the dolphin contains, like that of the horse, jecorin, cystine, a substance of the xanthine group, and glycogen. Cystine is a product of normal metabolism.

The substance (*gorgonin*) of the horny skeleton of *Gorgonia cavolinii* contains iodine in organic combination. On decomposition with barium hydroxide, gorgonin yields an amido-acid containing iodine (*iodogorgonic acid*, $C_4H_5NIO_2$), which is crystalline, and has the composition of an iodoamidobutyric acid; its constitution is, however, not yet certain.

The living substance of the *Gorgonia* contains no iodine or only the merest traces; it is of proteid nature, and, on decomposition with hydrochloric acid, yields lysine and probably lysatine.

Gorgonin is also a proteid; when decomposed with hydrochloric acid, it yields leucine, tyrosine, lysine, lysatine (?), iodogorgonic acid and ammonia.

W. D. H.

Analysis of Human Milk. By FRIEDRICH SÖLDNER and WILLIAM CAMERER (*Zeit. Biol.*, 1896, **33**, 43—71).—The analyses show that human milk contains less proteid matter than was previously supposed. 100 grams of milk collected, on the average, in the second week after parturition, contain 1.52 proteid, 3.28 fat, 6.5 sugar, 0.27 ash, 0.05 citric acid, 0.78 unknown extractives, 12.4 total dry residue. The unknown extractives, which are almost absent in cow's milk, are increased in the colostrum.

W. D. H.

Composition of the Milk Fat of the Cow, the Goat, and the Reindeer. By E. SOLBERG (*Bied. Centr.*, 1896, **25**, 15—17; from *Tidsskr. Norsk. Landbrug*, 1895, 300—338).—The following results were obtained with the fat obtained from cheese from (1) goat's milk and (2) reindeer milk.

	M. p.	Solidifying. point.	Sp. gr. at 15° (average).	Sp. gr. at 100° (average).	Refract. coefficient.	Acid number (milligrams KOH).
(1)	27—38·5	24—31	0·9312	0·8669	1·4596	3·95—13·88
(2)	37—42	34—39	0·9428	0·8640	1·4647	27·60
	Saponification. number.	Hehner's number.	Reichert's number.	Iodine number.	Lecithin per cent.	
(1)	221·6	86·46—87·34	23·1—25·4	30·4—34·6	0·1—0·2	
(2)	219·2	86·89	31·4	25·1	0·21	

Goat's milk fat resembles cow's milk fat a good deal, but the former contains more insoluble volatile acids than the latter. In reindeer milk fat, the amount of insoluble volatile acids is much less

N. H. J. M.

Excretion of Ammonia in Disease. By THEODOR RUMPF (*Virchow's Archiv*, 1896, **143**, 1—41).—In a number of cases of infective disease (pneumonia, typhoid, influenza, cholera, &c.), the amount of ammonia excreted in the urine, as such, is increased. The normal amount of nitrogen in the form of ammonia in the 24 hours' urine is given as varying from 0.4 to 1 gram. In the cases of disease examined, it varied from 0.8 to 6 grams. This condition passes off in an early stage of convalescence. The total nitrogen excreted is not similarly increased. On the average, there is an increase of 37 per cent. in the proportion of ammoniacal nitrogen to total nitrogen. The increase cannot be attributed to change of diet, but is explained as the result of the activity of micro-organisms. In cultures, addition of the bacilli of cholera and of other diseases causes a formation of ammonia. W. D. H.

Excretion of Ammonia in Disease. By E. HALLERVORDEN (*Virchow's Archiv*, 1896, **143**, 705—706).—A criticism of Rumpf's conclusions (preceding abstract). The ammonia produced by bacteria would be converted into urea. Ammonia has, above all, in the body, the function of an acid neutraliser; this is entirely neglected by Rumpf, who gives no estimations of acidity. The cause of the apparent increase of ammonia is doubtless to be sought in the alteration in the amount of acids produced by the fever. W. D. H.

Uric acid, Xanthine Bases, and Phosphoric acid in Human Urine. By WILLIAM CAMERER (*Zeit. Biol.*, 1896, **33**, 139—155).—Horbaczewski considers that an important source of uric acid in the urine is the xanthine bases, which are formed by the decomposition of nucleïn; phosphoric acid and proteïd are liberated at the same time. He explains the increase of uric acid after food as due to the increased decomposition of an increased number of white corpuscles (digestion leucocytosis). The present research was carried out with different diets, the ingesta and excreta (uric acid, urea, phosphoric anhydride, &c.) being analysed. The conclusion drawn, is that digestion leucocytosis is not a cause of increased excretion of uric acid, but that uric acid has two principal sources; it is a product of metabolism, and a product of the nucleïn taken in with the food, for instance, in calf's thymus (sweetbread). It is the increase or decrease of nucleïn in the food which causes a corresponding rise and fall in the uric acid secreted after a meal. W. D. H.

Excretion of Uric acid. By WILHELM EBSTEIN and ARTHUR NICOLAÏER (*Virchow's Archiv*, 1896, **143**, 337—368).—Administration of uric acid to dogs, with the food, produces no appreciable effect, and it is discoverable in the fæces; in rabbits, however, which normally secrete no uric acid, intravascular, subcutaneous, and intraperitoneal injection of this substance dissolved in solution of piperazine produced the following effects. The acid was rapidly removed from the seat of injection, and in a few cases nervous symptoms (increase of reflex irritability, paralysis followed by death) were noticed. The uric acid was excreted by the kidneys; this was most markedly the case

in those animals whose kidneys had been previously injured by the administration of aloïn, and here the acid was excreted in the form of sphæroliths. The excretion of this foreign substance caused a chronic nephritis in the kidneys of the healthy rabbits experimented with.

W. D. H.

Chemistry of Vegetable Physiology and Agriculture.

The Processes of Germination. By DM. PRIANISCHNIKOFF (*Landw. Versuchs-Stat.*, 1896, **46**, 459—470; compare Abstr., 1895, ii, 124).—Seedlings of *Vicia Faba*, 10 days old, were kept for 10 days longer in (1) 10 per cent. glycerol solution, in (2) 10 per cent. sugar, and (3) in water, respectively. Each solution contained also potassium phosphate, and calcium and magnesium sulphates. The presence of sugar soon began to hinder growth; in glycerol solution, the plants grew, but much less than in water. Sugar caused a distinct deposition of starch, whilst in glycerol, the starch production was very slight. In the plants grown in water, starch was detected in traces. Growth and deposition of starch thus vary inversely. The following analytical results are given, showing the changes in the amounts of nitrogenous constituents of the seedlings.

	Nitrogen in dry substance.			
	Total.	As proteids.	As amides.	As asparagine.
10 days in water	4.89	2.72	2.20	1.00
10 days in water and 10 days in sugar solution..	4.92	2.65	2.37	1.10
20 days in water	5.73	2.66	3.15	1.68

There was therefore no regeneration of asparagine, and it is very probable that asparagine is never regenerated in the dark. This was the view held by Boussingault, who looked on asparagine (in etiolated seedlings) as a product of oxidation of albumin, like urea in the animal organism (compare O. Müller, Abstr., 1887, 70).

It is not yet certain whether carbohydrates are formed in the decomposition of proteids; if they are formed, it is probable that they are products of hydration and not of oxidation.

The following calculations show the changes in 100 grams of seed (*Vicia sativa*) in germinating. The amount of ash was 3.27 per cent.

	Proteids.	Asparagine.	Amido- acids.	Organic bases.	Starch.	Soluble carbohydrates.
0 days..	28.50	(0.32)	(2.52)	2.25	37.82	5.59
10 „ ..	15.28	5.54	7.63	3.52	17.44	8.75
20 „ ..	10.60	7.86	10.19	2.62	9.93	7.67
30 „ ..	8.84	8.77	10.90	1.55	3.94	6.27
40 „ ..	8.86	9.92	10.57	1.50	2.59	4.05

	Ether extract.	Crude fibre.	Hemi- celluloses.	Loss of weight.	Not determined.
0 days..	0.80	6.64	4.70	0	7.59
10 „ ..	1.31	7.70	5.25	15.98	8.33
20 „ ..	1.20	9.15	5.80	24.26	7.45
30 „ ..	1.11	9.65	6.10	30.86	8.74
40 „ ..	1.07	10.98	6.40	34.09	6.70

The numbers for amido-acids were obtained by multiplying the nitrogen of the phosphotungstic acid precipitate by a coefficient corresponding with the mean between those of leucine and amido-valeric acids. Choline was assumed to be the only organic base.

N. H. J. M.

Nitrogen Assimilation by Plants. By J. H. AEBY (*Landw. Versuchs-Stat.*, 1896, **46**, 410—439).—Peas and mustard were grown in zinc, funnel-shaped vessels (25 cm. in diameter at the top and 20 cm. high), being kept under glass during rain. Two kinds of soil were employed: (1) garden soil (N = 0.4051 per cent.), and (2) loamy arable soil (two years with peas; N = 0.0688 and 0.0783 per cent.). The following were the experiments (with both soils): (1) fallow, (2) peas, (3) white mustard; (4), (5), and (6) same as (1), (2), and (3), respectively, but manured with calcium nitrate (N = 2 grams). In each experiment there were three or four pots each containing 4 kilograms of soil. The numerical results (averages in grams) are given in the table, p. 382.

As regards the experiments in garden soil, the mustard germinated well, but soon left off growing in the unmanured pot. The peas (in absence of nitrate) also showed signs of nitrogen hunger, but soon recovered. In arable soil, similar results were obtained. In both soils, and without application of nitrate, the peas grew luxuriantly, owing to nitrogen fixation by nodule bacteria; in garden soil (4 kilograms), 1.799 gram of nitrogen was gained, and in arable soil, 2.373 grams. Mustard, on the other hand, developed well only when supplied with nitrate, and in no case, even in presence of pea bacteria, was there any gain of nitrogen. The results of the experiments show very clearly the difference between the two plants, and the inability of mustard to fix free nitrogen, and are, therefore, opposed to those obtained by Liebscher (*Abstr.*, 1894, ii, 201). Pfeiffer and Francke (*Abstr.*, 1895, ii, 521) and Nobbe and Hiltner also concluded that white mustard does not utilise elementary nitrogen.

The methods employed and the analytical data are given in full.

N. H. J. M.

A Diastatic Ferment in the Sugar-beet (*Beta vulgaris*). By M. GONNERMANN (*Chem. Zeit.*, 1895, **19**, 1806).—Germinating and frozen beets were crushed to a fine pulp and shaken with water. The aqueous extract was then filtered, and precautions were taken to destroy all fermentative organisms; soluble calcium and lead salts were added, and precipitated by means of soda, in the hope of thus carrying down any enzymes present. The precipitates were separated by filtration, acidified with dilute acetic acid, and the solution thrown into 95 per cent. alcohol, and the precipitate produced was filtered

Nitrogen.										
Dry produce (including roots).	In soil at commence- ment.	In seeds.	Total initial.	In soil at conclusion.		In produce.	Total final.	Gain or loss.		
				As nitrate.	Organic.					
<i>In garden soil. (N = 0.4051 per cent.).</i>										
1. Fallow.....	—	13.286	—	13.286	0.303	12.694	12.997	12.997	—	—0.289
2. Peas.....	105.6	"	0.263	13.549	0.0	12.699	12.699	15.525	2.826	+1.976
3. Mustard.....	14.2	"	0.023	13.309	0.0	12.797	12.797	13.057	0.260	-0.252
4. Fallow.....	—	"	—	15.286*	2.132	12.902	12.902	15.034	—	-0.252
5. Peas.....	139.9	"	0.255	15.541*	0.355	13.043	13.393	17.162	3.764	+1.621
6. Mustard.....	91.1	"	0.023	15.509*	0.0	12.905	12.905	14.970	2.065	-0.339
<i>In arable loam. (N = 0.0688 per cent.).</i>										
1. Fallow.....	—	3.106	—	3.106	0.077	2.897	2.974	2.974	—	-0.132
2. Peas.....	105.0	2.831	0.265	3.078	0.0	3.072	3.072	5.837	2.765	+2.759
3. Mustard.....	3.2	3.106	0.023	3.129	0.0	3.040	3.040	3.101	0.061	-0.028
4. Fallow.....	—	3.106	—	5.106*	2.019	2.890	4.909	4.909	—	-0.197
5. Peas.....	148.8	2.831	0.265	5.078*	0.061	3.144	3.205	7.065	3.860	+1.987
6. Mustard.....	75.7	3.106	0.023	5.129*	0.0	3.192	3.192	4.979	1.787	-0.150

* Including 2 grains as calcium nitrate.

off, dried at 38°, and extracted with glycerol. The following facts show, beyond question, that the glycerol extract contained an enzyme.

When added to starch-paste, maintained at 38° for six hours, the presence of a reducing substance was detected; a similar experiment, carried out without the addition of the extract, showing no such result. Further experiments proved that amylopectin could be converted into dextrose by digestion with the glycerol extract during half an hour.

A. L.

Occurrence of Arginine in the Tubers and Roots of certain Plants. By ERNST SCHULZE (*Ber.*, 1896, 29, 352—354).—Arginine (compare *Abstr.*, 1886, 725) occurs in the tubers of the turnip (*Brassica rapa*), and of the artichoke (*Helianthus tuberosus*), and in the roots of *Ptelea trifoliata*. It is probably also contained in the roots of chicory. Dried turnips contain only 0.18 per cent. of arginine.

Arginine (from *Lupinus luteus*) was found to have no physiological action on animals.

C. F. B.

Coloration of the Tissues, and Juice of certain Fungi when exposed to Air. By EMILE E. BOURQUELOT and GABRIEL BERTRAND (*J. Pharm.*, 1896, [6], 3, 177—182).—The juice of various species of *Boletus* becomes coloured when exposed to air; this is due to the action of an oxidising ferment. Specimens of *B. cyaneus* are finely divided, with as little exposure to air as possible, and extracted with boiling alcohol (95 per cent.); the ferment is destroyed and the solution can be kept for an indefinite period without undergoing change, even when diluted with water or exposed to air; but when a fragment of *Russula cyanoxantha* or *R. furcata* is introduced into the alcoholic solution, diluted with an equal volume of water, the liquid rapidly turns blue, from the surface downwards; the same change is produced, as in the case of guaiacum tincture, by various oxidising agents, such as ferric chloride, sodium hypochlorite, and lead peroxide; the colour is destroyed by acids, with the exception of acetic, and by alkalis. The analogous compound from *R. nigricans* is insoluble in alcohol; it is prepared by treating the finely divided fungus with alcohol and extracting the residue with hot water; the solution is filtered hot, and, when cold, the compound crystallises in colourless, microscopic needles; in presence of the ferment, it gives first a purple, then an inky-black, solution, but the colour is not produced by ordinary oxidising agents.

J. B. T.

Composition of Medlars. By WILHELM BERSCH (*Landw. Versuchs-Stat.*, 1896, 46, 471—473).—The fruit of the common medlar (*Mespilus germanica*) has the following composition (per cent. in dry matter, p. 384).

The amounts of dry matter in the fresh substance are (1) 30.87, (2) 36.86, (3) 24.79, and (4) 61.58 per cent.

The fruit contains malic acid, acetic acid (0.03 per cent.), and alcohol.

	Protein.	Fat.	Sugar.	N-free extract.	Crude fibre.	Ash.
1. Whole fruit..	2.79	1.04	36.08	40.98	16.29	2.82
2. Skin.....	4.12	2.66	—	72.62	17.51	3.09
3. Flesh.....	2.62	0.57	48.56	37.63	7.35	3.27
4. Stones	2.55	0.62	—	46.66	48.52	1.65

N. H. J. M.

Composition of Different Melons. By WILHELM BERSCH (*Landw. Versuchs-Stat.*, 1896, **46**, 473—476).—The whole fruit (1) and the fruit flesh (2) of the different melons examined contained the following amounts of dry matter. Sugar melons (1) 7.148, (2) 4.850; Persican melons (1) 6.130, (2) 4.100; water melons (1) 6.56, (2) 6.31 per cent. The percentage composition of the dry matter is as follows.

		Protein.	Fat.	Dextrose.	N-free extract.	Crude fibre.	Ash.
Sugar melon ..	{ (1)	22.250	6.728	36.320	12.970	14.890	6.842
	{ (2)	13.394	1.694	70.632	0.289	6.897	7.094
Persican melon	{ (1)	20.710	13.140	30.180	4.485	21.550	9.935
	{ (2)	11.800	1.854	65.850	3.439	8.439	8.618
Water melon ..	{ (1)	13.740	6.890	37.360	21.740	15.410	4.860
	{ (2)	9.731	1.062	66.730	16.946	1.949	3.582

The sugar occurred entirely as dextrose.

N. H. J. M.

The Potash and Phosphoric acid required by Cultivated Plants. By SMETS and C. SCHREIBER (*Bied. Centr.*, 1895, **24**, 805—808; from *Recherches sur les besoins potas. et phosphat. des plantes cult. Masseyk.*, 1894; compare this vol., ii, 68).—The following numbers show the relative requirements for potash and phosphoric acid of the different plants.

	K ₂ O.	P ₂ O ₅ .		K ₂ O.	P ₂ O ₅ .
<i>Holcus lanatus</i>	16	40	<i>Secale</i>	39	70
<i>Phleum pratense</i>	18	58	<i>Vicia sativa</i>	46	79
<i>Avena elatior</i>	18	51	<i>Lucerne</i>	51	70
<i>Beta vulgaris</i>	23	64	<i>Trifolium pratense</i> ..	53	74
<i>Hordeum vulgare</i>	24	71	<i>Maize</i>	55	74
<i>Triticum spelta</i>	27	54	<i>Setaria german.</i>	56	47
<i>Lolium ital.</i>	28	49	<i>Ornithopus</i>	56	64
<i>Fagopyrum esculentum</i> .	29	45	<i>Trifolium repens</i>	63	76
<i>Faba vulgaris</i>	32	65	<i>Daucus carota</i>	64	74
<i>Pisum sativum</i>	34	61	<i>Cannabis sativa</i>	65	81
<i>Spergula arvensis</i>	38	52	<i>Trifolium incarnatum</i>	73	68

Greater differences are shown in the requirements for potash than for phosphoric acid. The gramineous plants require the least potash.

N. H. J. M.

Analytical Chemistry.

A Gas Pipette of Simple Construction. By ALEXANDER P. LIDOFF (*J. Russ. Chem. Soc.*, 1894, **26**, 37—39).—This apparatus consists of a short glass beaker of about 400 c.c. capacity, into which the absorption liquid is poured, and a funnel of 150 c.c. capacity put upside down into the beaker. The upper part of the funnel is blown into a small bulb, and a capillary tube fused on to it. A mark is made on the capillary tube, and the tube closed by a piece of india-rubber tubing and a Mohr's clip, connected with a graduated pipette. To increase the absorption of the gas by the liquid, 7—8 grams of asbestos or glass wool are placed in the beaker under the funnel. A copper or lead ring of about 10 grams weight is placed on the funnel to prevent its rising when filled with gas.

To protect the reagent from atmospheric action, a thin layer of paraffin oil, sp. gr. 0.875, is poured on it. The author claims that a perfect isolation of the reagent is thus effected.

This pipette is worked exactly like Hempel's, namely, the india-rubber tube of the pipette, which is filled up with the liquid to the mark, is connected by means of a bent capillary tube with the gas burette, the gas from the burette pressed into the pipette, and the latter closed with the Mohr's clip.

The shaking of the ordinary gas pipette is in this case replaced by moving the funnel up and down in the liquid.

A further advantage of this apparatus is the possibility of heating the absorbent in the beaker if necessary. S. G. R.

A New Cyanometric Method and its Applications. By GEORGES DENIGÈS (*Ann. Chim. Phys.*, 1895, [7], **6**, 381—428).—The author first, from thermochemical considerations, concludes that the addition of an alkali chloride as an indicator in the Liebig estimation of cyanides can be of no advantage; he then shows by actual experiment that this is so, as the permanent precipitate which is formed always consists of silver cyanide, and not of silver chloride. If an alkali bromide is added, the precipitate formed consists of silver cyanide with a little silver bromide.

The author's method consists in using 10 drops of a 20 per cent. potassium iodide solution as an indicator, in a medium which has been rendered strongly alkaline with ammonia. The silver cyanide is readily soluble in ammonia, whereas silver iodide is not. N/10 silver nitrate is therefore run into the solution until a slight permanent precipitate is formed. The calculation is the same as in the usual Liebig titration, two molecules of potassium cyanide reacting with one of silver nitrate. The amount of ammonia present has but little influence on the reaction; sodium carbonate also, or moderate quantities of alcohol do not interfere with the titration. Cherry laurel water can also be titrated in a similar manner; in this case, however, it is necessary to add a few c.c. of caustic soda or

potash before the ammonia. If this precaution is not taken, the amount of cyanide found varies with the length of time during which the mixture is allowed to remain (compare Gregor, *Abstr.*, 1894, ii, 165). This result is no doubt due to the condensation, in the presence of ammonia, of part of the hydrocyanic acid with the benzaldehyde, which also occurs in the distillate.

The method can also be used for the estimation of alkali cyanides and cyanides which are decomposed by alkalis; if these contain any sulphide, as many commercial cyanides do, it is necessary to remove the sulphide by treatment with zinc sulphate in the presence of sodium hydroxide; the excess of sulphate can be removed by lead acetate, and the filtrate then titrated, after the addition of 10 drops of the potassium iodide solution, with standard silver nitrate. Mercuric cyanide can also be titrated if it is first decomposed with sodium sulphide and the excess of sulphide removed as above.

The author recommends this method for the estimation of silver in the form of any of its salts. The silver salt is dissolved in water, ammonium hydroxide, N/10 potassium cyanide, or nitric acid, according to its solubility, a slight excess (5—10 c.c.) of ammonium hydroxide and 20 c.c. of N/10 potassium cyanide are then added, and the excess of cyanide is estimated by the method described above. The N/10 cyanide solution can be accurately prepared by titrating against N/10 silver nitrate, and the author finds that such a solution, previously rendered alkaline by ammonia, or, still better, by caustic soda, is extremely stable, and may be kept for months. To estimate silver in the presence of copper or mercury, it is better to precipitate the silver as chloride, to dissolve the well washed chloride in ammonia and N/10 potassium cyanide, and to titrate as above.

The same principles may be made use of for the estimation of chlorides in various organic liquids, such as bile, urine, gastric juice, cystic fluids, blood, milk, wine, vinegar, and other fermented liquids. In the case of bile, 20 c.c. of the bile, 2 c.c. of nitric acid, and 20 c.c. of N/10 silver nitrate are placed in a 200 c.c. flask, and made up to the mark with distilled water. After filtration, 100 c.c. of the clear filtrate is mixed with 15 c.c. of ammonia, 10 drops of the 20 per cent. potassium iodide solution, and 10 c.c. of the N/10 potassium cyanide, and then titrated back with N/10 silver nitrate. If n = the number of c.c. of N/10 silver nitrate used, then $n \times 0.585$ gives the amount of chloride, expressed as sodium chloride, contained in 1 litre of the bile.

For urine, it is generally necessary to work with a less concentrated solution, and if the urine contains much proteid matter it is advisable to warm on the water bath for 10—15 minutes before making up to the requisite volume. For blood, it is best to mix with an equal volume of a cold saturated sodium fluoride solution and 10 c.c. of pure nitric acid before dilution.

Bromides and mixtures of bromides and chlorides may be estimated in a similar manner. For the estimation of iodides, the author recommends the following method. 50 c.c. of approximately N/10 iodide solution is taken, added to 25 c.c. of ammonia, 5 c.c. of hydrochloric

acid, and 50 c.c. of N/10 silver nitrate, and then made up to 250 c.c. with distilled water. Unless hydrochloric acid is added, the silver iodide is obtained in too fine a state of division to allow of filtration. 200 c.c. of the clear filtrate is added to 10 c.c. of N/10 potassium cyanide and 10 drops of the indicator (20 per cent. potassium iodide solution), and the excess of cyanide estimated in the usual way. Iodates, after conversion into iodides by treatment with sodium hydrogen sulphite, may be titrated in the same way. Many organic iodo-compounds may be treated in a similar manner; the iodine is converted into iodic and hydriodic acids by boiling for one to two minutes with a mixture of 1 c.c. of nitric acid and 2 c.c. of hydrochloric acid. The iodic acid can be reduced to hydriodic acid by means of sodium hydrogen sulphite, and then titrated as above. In certain cases, it is preferable to warm the iodo-compound with about 1 c.c. of concentrated sulphuric acid.

The same method can also be used indirectly for the estimation of xantho-uric derivatives in urine, and of theobromine in the presence of caffeine. In both cases, the silver compounds are precipitated by means of ammoniacal silver nitrate, and the excess of silver nitrate in the filtrate is then estimated by the method already described.

The author finally recommends this method for the indirect estimation of substances which precipitate metallic silver from solutions of silver nitrate. Thus, hydrogen arsenide may be estimated by passing it into a solution of N/10 silver nitrate acidified with nitric acid, filtering off the metallic silver formed, and then estimating the amount of silver nitrate left in the filtrate after it has been rendered alkaline by ammonia. Hydroxylamine and phenylhydrazine reduce ammoniacal silver nitrate, and may therefore be estimated in a similar manner. 0.08—0.10 gram of the hydroxylamine salt, 25 c.c. of N/10 silver nitrate, 10 c.c. of ammonia, and 2 c.c. of caustic soda are placed in a 125-c.c. flask and heated to boiling; after cooling, the volume is made up to the mark with distilled water, the metallic silver is filtered off, and the excess of silver nitrate in 100 c.c. of the filtrate estimated as before.

J. J. S.

[**Estimation of Sulphur by combustion in Air.**] By CHARLES F. MABERY (*Amer. Chem. J.*, 1896, **18**, 149—151).—The author believes this method, which he recently described (*Abstr.*, 1895, ii, 136), is not excelled in accuracy by any other method at present in use. It is applicable to non-volatile substances. Substances containing a high percentage of sulphur may yield sulphurous as well as sulphuric acid; in such cases a little hydrogen peroxide should be added before titrating.

Estimation of Sulphur in Illuminating Gas and in Coal. By CHARLES F. MABERY (*Amer. Chem. J.*, 1896, **18**, 207—213).—This is a modification of a method previously described by the author (*Abstr.*, 1895, ii, 136). The current of gas is measured by a meter, and is burnt at a constriction in a combustion tube 45.5 cm. long, having the constriction 30 cm., from the forward end. A rapid current of air is drawn through the combustion tube. The products of

combustion and the excess of air are drawn through a large U-tube containing a centinormal solution of sodium hydroxide, in which the sulphuric acid is absorbed. Subsequent titration of this solution with centinormal sulphuric acid gives the amount of sulphur present in the gas. Since treatment of this solution with hydrogen peroxide in no way affected the result, the author is convinced that all the sulphur is completely oxidised to sulphuric acid by this method.

In Coal.—The coal is weighed in a platinum boat sufficiently large to contain all the ash, and placed in the forward portion of the combustion tube, air being drawn both through an inner hard-glass tube terminating at the constriction of the combustion tube, and, in a slower current, through a tube at the rear. A U-tube of considerable size is employed, and a decinormal solution of sodium hydroxide used.

Determinations conducted on the ash of several varieties of coal treated in this manner gave a mean of only 0.043 per cent. of sulphur. The combustion is, therefore, practically complete.

J. F. T.

Standardising Potassium Permanganate and Sulphuric acid. By HARMON N. MORSE and A. D. CHAMBERS (*Amer. Chem. J.*, 1896, 18, 236—238).—It is possible, by means of a standard solution of potassium permanganate of normal composition, in the presence of a neutral reducing agent such as hydrogen peroxide, to accurately determine the strength of a dilute solution of sulphuric acid, and conversely by means of standard sulphuric acid, to standardise a solution of potassium permanganate.

J. F. T.

Volumetric Estimation of Phosphorus. By LINDEMANN and MORTEU (*Bull. Soc. Chim.*, 1896, [3], 13, 523—533).—The phosphoric acid is separated as ammonio-manganous phosphate, and the manganese then converted into the dioxide, and estimated volumetrically.

Soluble phosphates, such as alkali phosphates, are dissolved in water (0.1 gram P_2O_5 in 50 c.c.), ammonium chloride (10 c.c. of 20 per cent. solution) and ammonia (10 c.c.) are added, and then ammonium citrate (25 c.c. of solution containing 150 grams of acid and 500 c.c. of ammonia to 1000 c.c. of water). The phosphoric acid is next precipitated by the addition of manganous sulphate (25 c.c. of 25 per cent. solution of the hydrated salt), the double salt appearing in large, nacreous, rose-coloured crystals on boiling, provided the solution is gently stirred and care taken to avoid rubbing the sides of the vessel. In the presence of ammonium citrate, the precipitation is as complete in a few minutes as in the presence of excess of phosphate, and the excess of manganese, of course, remains in solution.

The precipitate is collected and redissolved in dilute hydrochloric acid in the vessel in which it was first precipitated, and after dilution (to 250—300 c.c.), hydrogen peroxide is added in amount (1—4 c.c.) proportional to the amount of the precipitate; the solution is then made alkaline with potash (20 c.c. of 10 per cent. solution), and boiled for 10 minutes to expel the excess of hydrogen peroxide. When cold, the precipitated manganese dioxide is redissolved in hydrochloric

acid (20 c.c. of 20 per cent. acid), and after a short interval, excess of potassium iodide (20 c.c. of 10 per cent. solution) is added.

Finally, the iodide thus liberated is titrated with N/20 sodium thiosulphate, of which 1 c.c. = 0.0023 gram P_2O_5 . A correction of 4 milligrams must be added to the amount of phosphoric anhydride found, to allow for the slight solubility of the ammonio-manganous phosphate in the reagents.

Insoluble phosphates are first dissolved in acids in the usual way and precipitated with ammonium molybdate, the precipitated phosphomolybdate being then redissolved in dilute ammonia (10 c.c. to 50 c.c. of water), and treated in the same way as a soluble phosphate.

JN. W.

The Molybdic Reagent. By G. MEILLÈRE (*J. Pharm.*, 1896, 3, 61—62).—This reagent is prepared by mixing ammonium molybdate solution (15 per cent., 200 c.c.) with sulphuric acid (1 : 1, 20 c.c.), and adding concentrated nitric acid (30 c.c.). The reagent is very sensitive, can be heated at 100° for a short time without decomposition, and may even be employed for the direct estimation of phosphoric acid. In this case, the precipitate is gently warmed, allowed to remain during 12 hours, and then washed with a little saturated solution of ammonium nitrate; under these conditions, molybdic acid is only deposited in traces, and unless a high degree of accuracy is required, it is unnecessary to subsequently employ magnesia mixture and ammonium citrate.

Arsenic acid is precipitated less readily than phosphoric acid, and the precipitate is less homogeneous on account of the more prolonged heating which is required; the precipitate is redissolved, and precipitated by means of magnesia mixture in presence of ammonium citrate; the presence of tartrates is undesirable, as they retard the deposition of the arsenate.

J. B. T.

Estimation of Phosphorus in Iron and Iron Ores containing Titanium. By JOHN PATTINSON and HUGH S. PATTINSON (*J. Soc. Chem. Ind.*, 1895, 14, 443—444).—The authors have noticed that the formation of the yellow molybdic precipitate is seriously interfered with by the presence of titanous acid, and that this substance must, therefore, be first removed.

This is best effected by a method communicated to the authors by Stead. The iron is first reduced, as usual, to the ferrous state, and enough alum is then added to combine with all the phosphoric acid, and in this way aluminium phosphate is precipitated instead of the iron compound; this is then fused with sodium carbonate and extracted with water, which will leave any sodium titanate insoluble. The solution contains all the phosphoric acid, which is estimated in the usual manner.

L. DE K.

Application of the Citrate Process to Wagner's Method for the Estimation of Citrate Soluble Phosphoric acid in Basic Slags. By F. MACH and MAX PASSON (*Zeit. angew. Chem.*, 1896, 129).—To avoid the troublesome molybdate separation, the authors operate as follows: 100 c.c. of Wagner's solution is boiled in a half-litre flask

with a very long narrow neck, with 10 c.c. of sulphuric acid, 15 c.c. of strong nitric acid, and a drop of mercury until the liquid has become quite colourless. After cooling, 20 c.c. of a 10 per cent. sodium chloride solution is added to precipitate the mercury, the mixture is diluted to 200 c.c., and 100 c.c. of the filtrate is mixed with 100 c.c. of the conventional ammonium citrate solution. After cooling, 25 c.c. of magnesium mixture is added to precipitate the phosphoric acid.

L. DE K.

Detection of Chromates and Arsenates. By UBALDO ANTONY (*Gazzetta*, 1895, 25, ii, 407—408).—The author criticises Tarugi's remarks (this vol., ii, 340) respecting Tassinari and Antony's book on qualitative analysis and the detection of arsenates in presence of chromates.

W. J. P.

Estimation of Arsenic in Crude Sulphuric acid. By GEORG HATTENSAUR (*Zeit. angew. Chem.*, 1896, 130—131).—Five hundred c.c. of the sample is diluted with 500 c.c. of water, and, after cooling, 500 c.c. of dilute hydrochloric acid (1—2) is added. This prevents the precipitation of lead sulphate, and also the subsequent formation of lead sulphide.

The arsenic is now precipitated by a current of hydrogen sulphide, and is collected on a weighed filter and weighed as sulphide. If the amount is not too small, it may also be converted, in the usual way, into magnesium pyroarsenate and weighed as such.

L. DE K.

Estimation of Arsenic in Iron Ores, Steel, and Pig-Iron. By JOHN E. STEAD (*J. Soc. Chem. Ind.*, 1895, 14, 444—446).—The steel is dissolved in dilute hydrochloric acid, and the gas evolved is passed through bromine water (or through a solution of silver sulphate), the apparatus being fitted with a potash tube to prevent escape of bromine vapours. The potash solution is afterwards acidified with hydrochloric acid and added to the bromine water, which is boiled until colourless and then added to the iron solution in the flask; if silver sulphate has been used, it is first precipitated with hydrochloric acid, and then added to the iron solution.

The liquid is now mixed with about half a gram of zinc sulphide, which soon causes a precipitate containing all the arsenic. This is collected, dissolved in bromine water, and after boiling off any excess of bromine, it is put into a retort and distilled with ferrous chloride and hydrochloric acid; to ensure the complete expulsion of the arsenic, however, it is necessary to distil a few times with fresh hydrochloric acid. If there are not many samples to test, the precipitation as sulphide may be omitted, and the liquid at once distilled to dryness. The distillate is neutralised with ammonia, again slightly acidified with hydrochloric acid, mixed with a slight excess of sodium carbonate, and then titrated with a weak standard solution of iodine, using starch as indicator.

Pig-iron is treated in the same manner, omitting the precipitation as sulphide. Iron ores are simply distilled with hydrochloric acid and ferrous chloride.

L. DE K.

Estimation of Free and Combined Carbonic Anhydride in Carbonated Waters (Vichy-Vals). By G. MEILLÈRE (*J. Pharm.*, 1896, [6], 3, 6—8).—To estimate the total carbonic anhydride, the water under examination is mixed with an equal volume of baryta water of known content. Waters rich in carbonic anhydride are siphoned as completely as possible from the bottle to the bottom of the vessel containing the baryta water, and the bottle is then rinsed with baryta solution, care being taken to avoid loss of gas. An aliquot part of the liquid is filtered and titrated with normal acid, using tropæolin as an indicator; this gives the total carbonic anhydride. For the combined carbonic anhydride, the original water is titrated directly with acid and tropæolin. The method gives very satisfactory results, and is much more readily carried out than one based on the extraction of the gas under reduced pressure. J. B. T.

Exclusion of Ammonium Sulphide from Qualitative Analysis. By N. TARUGI (*Gazzetta*, 1895, 25, ii, 478—481).—In order to avoid the inconveniences attending the use of ammonium sulphide in precipitating the metals of the fourth group in qualitative analysis, the author proposes to replace it by ammonium ferricyanide. The filtrate from the precipitate obtained with ammonia and ammonium chloride is boiled, slightly acidified with hydrochloric acid, a slight excess of ammonium ferricyanide added, and the liquid heated; the precipitate (A) contains the cobalt, nickel, and manganese as ferricyanides insoluble in dilute hydrochloric acid. The filtrate is treated with ammonia and ammonium carbonate, and the precipitate (B) containing only carbonates of barium, strontium, and calcium is filtered off. Ammonium phosphate is then added to the filtrate, and the precipitate (C), containing all the magnesium, separated; if a yellowish precipitate is obtained on adding acetic acid to the filtrate from C, it can only consist of zinc ferricyanide. The filtrate can be dried and heated to redness, and the residue examined for the alkali metals in the usual way.

The precipitate A is shaken with cold ammonia and filtered; if the filtrate gives a yellowish precipitate or turbidity on acidifying with hydrochloric acid, nickel is present, the ferricyanide of this metal being insoluble in hydrochloric acid but very soluble in ammonia. The residue left on the filter may contain manganese and cobalt; the presence of the former may be detected by heating with lead dioxide and nitric acid and examining for permanganic acid, or by fusing a part of the precipitate with potassium nitrate and carbonate on a platinum spatula, and observing if a green colour is produced; cobalt may be detected by examining in a bead in the reducing flame. A very delicate test for the presence of cobalt and manganese in the precipitate left after extracting the nickel as above, consists in drying it, heating to redness, and repeatedly extracting the residue with very dilute hydrochloric acid until it is no longer coloured yellow. The residue is then boiled with concentrated hydrochloric acid, and the solution evaporated to dryness, dissolved in water, and potassium cyanide added until re-solution of the precipitate occurs; a few drops of potassium nitrite and one drop of nitric acid are then

added; if the solution contains a trace of cobalt, it becomes tinted rose colour, but if manganese alone is present, a greenish precipitate is formed, whilst the solution remains colourless. If both metals are present, both coloration and turbidity occur together.

The precipitate B is examined in the usual way for barium, strontium, and calcium, and the presence of magnesium in C is also confirmed by the ordinary method.

W. J. P.

Estimation of Alkali Salts in Fireclays, Manures, &c. By ALEXANDER CAMERON (*J. Soc. Chem. Ind.*, 1895, **14**, 427—428).—The author has proved by several experiments that the barium hydroxide process is thoroughly trustworthy for the estimation of alkalis in manures, even in the presence of magnesia. The sulphate and carbonate methods may also be successfully employed, but the chloride method, on account of its troublesome nature and untrustworthy results, cannot be recommended.

L. DE K.

The Testing of Hydraulic Cements. By W. HARRY STANGER and BERTRAM BLOUNT (*J. Soc. Chem. Ind.*, 1894, **13**, 455—461).—The authors state that a chemical analysis alone is not sufficient to judge the quality of a sample of cement, but that several mechanical tests should be applied.

As regards the fineness, it has been recently recognised that the coarser particles of a hydraulic cement, at least, all that remain on a sieve having 76 meshes per linear inch, are wholly inert, or so slow in setting as to be practically useless. Good cement should not contain more than 10 per cent. of such coarse matter. The weight per unit measure is often, but erroneously, confused with the specific gravity of the sample, but that there is no connection between the two will be seen from the fact that a bushel of good cement weighs from 108—110 lbs., corresponding with an apparent specific gravity of 1.37, whilst the true specific gravity is about 3.15. As regards the well known test of tension and compression, the authors remark that the best cement may be rendered useless by admixture with bad sand and aggregate. Deval's hot process for the testing of soundness is considered to be too severe. The time of setting is much influenced by the temperature, being shorter as the latter increases, although there appears to be no definite relation. Finally, the authors point out that in the chemical analysis no good process for the estimation of free lime exists as yet, and that analyses showing over 1 per cent. of this substance should be received with caution. The hydraulic cements are themselves decomposed by water, and yield a liquid containing free lime.

L. DE K.

Colorimetric Estimation of Iron. By GEORG LUNGE (*Zeit. angew. Chem.*, 1896, 3—5).—The process is chiefly devised for the estimation of traces of iron in commercial aluminium sulphate. The reagents are a 10 per cent. solution of potassium thiocyanate, pure ether, and a solution of 8.606 grams of ammonium iron alum in a litre of water; this solution must be diluted to 10 times its volume immediately before use.

One or two grams of the sample is dissolved in a little water and heated for a few minutes with 1 c.c. of nitric acid free from iron; after cooling, the solution is made up to 50 c.c. 5 c.c. is then introduced into one of a set of glass stoppered cylinders, marked 25 c.c., and divided to 0.1 c.c., with plenty of room for shaking. 5 c.c. of dilute nitric acid (1 in 50) is put into a second cylinder, and, say, 1 c.c. of the iron solution is added; into the first cylinder a quantity of water equal to the iron solution in the second should then be introduced. Both liquids are now mixed with 5 c.c. of the thiocyanate solution; they both turn reddish, but the colour is no criterion of the relative amount of iron. 10 c.c. of ether is now added, and both tubes are thoroughly shaken, when a great difference in the colour of the ethereal layers will at once tell whether too much or too little iron solution has been added. The experiment is then repeated, using four tubes, and introducing slightly different amounts of iron solution in each. The comparison of the colours should not be attempted until a few hours have elapsed. The test is capable of showing with certainty 0.000001 gram of iron. L. DE K.

Analysis of Used Liquors in Chrome Tannage. By CARLTON B. HEAL and HENRY R. PROCTER (*J. Soc. Chem. Ind.*, 1895, **14**, 248—252).—The authors have investigated the action of skins on the solution of potassium dichromate, known as the dichromate bath, and also their behaviour in the hypo-bath (solution of sodium thiosulphate), and have tabulated the results.

The amount of free chromic acid in the dichromate bath may from time to time be titrated by adding a few drops of solution of 5 per cent. copper sulphate, boiling and running in standard soda until a brownish precipitate of basic copper chromate forms. This method, although not well adapted for turbid liquors, is nevertheless better than the hydrogen peroxide ether process, and can be used with artificial light. Titration with standard thiosulphate, using potassium iodide and a little hydrochloric acid in the chrome solution, and starch as indicator, also gives good results. L. DE K.

Estimation of Pentoses and Pentosans by the Furfuraldehyde Distillation Process. By F. MANN, M. KRÜGER, and BERNHARD TOLLENS (*Zeit. angew. Chem.*, 1896, **33**—46).—The first part of the paper by MANN and TOLLENS is devoted to an exhaustive examination of the phenylhydrazine method for estimating furfuraldehyde (*Abstr.*, 1893, **ii**, 52). The authors come practically to the same conclusions as Flint and Tollens, and also confirm the statement of Günther and others that furfuraldehyde is produced on distilling glycuronic acid or its derivatives with hydrochloric acid, although these compounds do not belong to the true pentoses (*Abstr.*, 1895, **ii**, 335). Experiments to increase the yield of furfuraldehyde by the addition of stannous chloride, or by substituting phosphoric for hydrochloric acid, were not successful.

The second part of the paper by KRÜGER and TOLLENS is an exhaustive study of the method proposed by Counciler (*Abstr.*, 1895, **ii**, 144), which involves the use of phloroglucinol. This process seems

to be preferable to the phenylhydrazine method, as it is not necessary to neutralise the distillate.

L. DE K.

Hydrolysis and Estimation of Sugar. By JAMES O'SULLIVAN (*J. Soc. Chem. Ind.*, 1895, **14**, 555—556).—See this vol., i, 334.

Specific Gravity of Milk-serum; Estimation of Lactose in Milk. By ED. VON RAUMER and ED. SPAETH (*Zeit. angew. Chem.*, 1896, 46—49; 70—73).—Two hundred c.c. of the sample is put into a beaker with a glass rod, and the whole carefully counterpoised on a balance capable of showing about 0.005 gram. After adding 2 c.c. of 20 per cent. acetic acid, the beaker is placed in boiling water for half an hour, and when cold, the loss in weight is carefully compensated by dropping in water from a pipette. After thoroughly mixing, the liquid is filtered through a folded filter, the first few c.c. which generally run through turbid being returned to the filter; if the filtrate cannot be obtained clear, a weighed portion of it must be heated again in a covered beaker, and the slight loss made good by adding a very thin alumina cream. A perfectly clear filtrate can then always be obtained.

A large number of experiments tabulated by the authors show that the sp. gr. of normal milk-serum varies from 1.026—1.033. As regards the estimation of the lactose, the authors recommend the gravimetric process of Soxhlet-Allihn, after clearing the milk, or its serum, by means of copper sulphate and aqueous potash. Estimation by means of the polariscope is not to be recommended, for although some of the results corresponded very well with those obtained by the copper process, some milks appear to contain a small quantity of a dextrin-like substance, which utterly upsets polarimetric observations. The amount of lactose in normal milk varies from 4.25 to 5.20 per cent.

L. DE K.

Polarisation and Analysis of Black Beers, Worts, and Caramel. By JOHN HERON (*J. Fed. Inst. Brewing*, 1895, **1**, 110—116).—The chief point in this paper is the method advocated for determining the rotatory power of black beers, worts, and solutions of caramel. For this purpose, 25 c.c. of the liquid is introduced into a 50-c.c. measuring flask and 5 c.c. of bleach solution added; when the liquid has become decolorised, which occurs in about five minutes, it is made up to bulk and filtered. Its rotatory power is then determined and multiplied by 2 to correct for dilution. Several experiments are described showing that bleaching liquor in the proportion recommended has no influence on the rotation of the more commonly occurring carbohydrates.

The method, sometimes advocated, of diluting black beers to 10 times their volume for taking their rotation, is condemned by the author as inaccurate.

A. K. M.

The Analysis of Beer, with some Remarks on the Unfermentable Reducing Residue. By G. HARRIS MORRIS (*J. Fed. Inst. Brewing*, 1895, **1**, 125—139).—The recognition of the fact that beer

contains an unfermentable residue which reduces Fehling's solution has necessitated some modification of the methods of analysis. The results obtained by the method described are expressed as percentages on the original wort solids and in the following terms. Matter fermented, low type maltodextrins (calculated as maltose), combined maltose and combined dextrin (constituting the normal maltodextrins), free dextrin, unfermentable reducing residue (calculated as maltose), and undetermined matter (by difference).

In order to carry out these determinations, 200 c.c. of the beer is evaporated to about one-half to expel the alcohol, and the residue made up to the original bulk; different portions are then treated as described under (a), (b), and (c).

(a) *Degradation with Cold Malt Extract*.—50 c.c. is digested for one hour at 55° with 2.5 c.c. of cold-water malt extract; it is then boiled, cooled, made up to 100 c.c., and filtered. Its reducing and rotatory powers are then determined in the ordinary way. A blank experiment with malt extract is also made and applied as a correction. (b) *Fermentation*.—In order to determine the low type maltodextrins, another portion of the residue (50 c.c.) is fermented with about 0.25 gram of pressed yeast at 20°. After about 72 hours, fermentation will have ceased, and the liquid is then cooled, a little alumina added, and the whole made up to 100 c.c.; it is then filtered and the reducing power determined. (c) *Fermentation in the Presence of Cold-water Malt Extract*.—Another 50 c.c. is fermented as under (b), but with the addition of 2.5 c.c. of cold-water malt extract, and both the reducing and rotatory powers of the product are estimated, these being corrected by means of a control experiment with the cold-water malt extract.

In calculating the results, the low type maltodextrins are arrived at by deducting the reducing power (expressed as CuO) obtained under (b) from the original reducing power of the beer and calculating the difference into maltose. The combined maltose is obtained by deducting the reducing power found from (c) from that given by (b). The increase in the reducing power after degradation with malt extract gives the combined dextrin, whilst the free dextrin is calculated from the rotation after degradation minus that due to the total maltose and the unfermentable residue. Finally, the reducing power given by (c) is calculated as maltose and expressed as unfermentable residue. The other determinations are carried out in the usual way, and need no description.

A. K. M.

Estimation of the Dry Substance in Malt Wort and Beer. By H. ELION (*J. Fed. Inst. Brewing*, 1895, 1, 23—28).—The method devised by the author depends on the use of dry air under diminished pressure and at a temperature of 97°, and may be used for determining the dry matter in wort, beer, yeast, malt, barley, sugar, &c. The apparatus consists of a jacketed cylinder arranged horizontally, and which can be heated either by steam or boiling water. The air within the cylinder is reduced to 40—50 mm. pressure, and a little air dried by sulphuric acid is then admitted. The material to be dried is placed in short, wide, cylindrical weighing bottles fitted with stoppers.

Results are given showing that the method compares favourably with those in which an absorbent material such as chrysotile or blotting paper is made use of. A. K. M.

Estimation of the Extract of Malt. By ARTHUR L. STERN (*J. Fed. Inst. Brewing*, 1895, 1, 448—450).—Two similar quantities (50 grams each) of ground malt are mashed in the usual way and then cooled. About 150 c.c. of water is added to one of the mashes, and both are weighed, the difference being the weight of the added water. The two products are then filtered, and from the specific gravities of the two filtrates the extract yielded by the malt can be calculated. For this purpose, the following formula is made use of.

$$V = \frac{SG' - 1}{SG' - SG''} \times A, \text{ in which}$$

SG' is the specific gravity of the solution before dilution.

SG'' " " " " " after " "

V is the volume of the solution before dilution.

A " weight or volume of the water added.

From the volume and specific gravity of the undiluted mash, the extract is calculated in the usual way. A. K. M.

Estimation of Alkali Benzoates. By G. REBIÈRE (*J. Pharm.*, 1896, [6], 3, 113—116).—The base is estimated by adding to the substance hydrochloric acid in excess, heating on the water bath until all free acid is removed, and titrating the residual chloride by means of N/10 silver nitrate solution. The benzoic acid is determined in a second and equal portion, which is dissolved in water (50—60 c.c.), and sulphuric acid (N/10) added, in the exact quantity needed to combine with the metal; the liberated benzoic acid is then titrated with soda (N/10), phenolphthaleïn being used as indicator. With normal benzoates, the quantity of soda required is equal to that of the sulphuric acid employed, whilst with basic and acid salts, it is less and more, respectively. After proving the accuracy of this method, the author investigated the composition of various benzoates employed in pharmacy. Sodium benzoate crystallises with 1H₂O, and is usually tolerably pure, the potassium salt contains 3H₂O, and generally has an acid reaction, the lithium salt contains 1H₂O, its analysis requires care to avoid loss of lithium chloride, whilst the ammonium salt is anhydrous; the ammonia is estimated by boiling with excess of the above soda solution, and titrating with sulphuric acid.

J. B. T.

Estimation of Parasulphanilic acid. By KARL BRENZINGER (*Zeit. angew. Chem.*, 1896, 131—133).—The process is based on the fact that the para-acid when treated with bromine water yields the theoretical amount of sulphuric acid, whilst the meta-acid does not yield any.

For the estimation of pure parasulphanilic acid, 17.3 grams of the sample is dissolved in water, and made up to a litre; 100 c.c. of this solution is, if at all alkaline, slightly acidified with hydrochloric acid and mixed with saturated bromine water until a drop of the

liquid gives a blue spot on potassium iodide-starch paper. After 20 minutes, the liquid is rendered faintly alkaline with aqueous soda, gently warmed for a short time, and the sulphuric acid estimated in the filtrate, as usual, by precipitating with barium chloride. If free sulphuric acid is present, it must be estimated by precipitating a known quantity of the original compound with barium chloride, and deducting the amount from the total acid.

The estimation of parasulphanilic acid in presence of metasulphanilic acid is effected in the same way as with the pure substance; the precipitation with barium chloride must, however, be effected at a boiling heat, and the precipitate washed with boiling water without delay.

L. DE K.

Acidity of Urine. By E. LÉPINOIS (*J. Pharm.*, 1896, [6], 3, 8—16).—The methods proposed for the estimation of the acidity of urine are enumerated and discussed; the presence of sodium dihydrogen phosphate, disodium hydrogen phosphate, sodium sulphate, and sodium chloride, alone or together, have no effect if potash is used for the titration, but they slightly influence the results if baryta water is employed. It is preferable to add alkali in excess and then titrate with acid, rather than to titrate with alkali directly, as in the former case the end point is observed more easily. It has been previously shown that if the urine is heated, the acidity is greater than at the ordinary temperature, this is probably caused by the alkali liberating ammonia; phosphates have an opposite effect; the observed difference in the titration values is the resultant of these effects. The most trustworthy results were obtained as follows: The urine (25 c.c.) is diluted with water (1—2 parts), according to its colour, phenolphthaleïn added, and then potash (10—15 c.c., N/4), the excess of the latter being titrated with hydrochloric acid (N/4). The observation of the end of the reaction is facilitated by treating a second and equal quantity of urine with water and alkali only, and comparing the colours.

J. B. T.

Volatile Acids of Wines. By HENRY JAY (*Bull. Soc. Chim.*, 1896, [3], 13, 642—644).—The sample is distilled in a current of steam for 1—1½ hours, and the distillate titrated with alkali. The amounts found in various genuine French and Spanish wines varied between limits corresponding with 0.38 to 0.8 gram of monhydrated sulphuric acid per litre. Algerian wines usually contain more than this, and are thus easily recognised.

JN. W.

Simultaneous Estimation of Organic and Inorganic Acidity in Beetroot Juice. By D. SIDERSKY (*Compt. rend.*, 1895, 121, 1164—1165).—Paper treated with a 0.1 per cent. aqueous solution of Congo red 4R gives a deep blue stain with a drop of a dilute inorganic acid, but is not affected by organic acids. If therefore beetroot juice is titrated with an alkali until a drop of the solution no longer gives a blue stain on the Congo red paper, the proportion of sulphuric acid is determined, and if the addition of alkali is then continued until the liquid ceases to be acid to litmus, the organic acids can be estimated.

Beetroot juice becomes dark brown when exposed to air, but this change is prevented by the presence of sulphuric acid. If, therefore, standard alkali is added to the liquid, with constant agitation, until the brown colour ceases to disappear, the sulphuric acid can be determined. Further addition of alkali with litmus paper as an indicator will give the quantity of organic acids.

C. H. B.

Analysis of Fats: Colour Reactions. By JULIUS LEWKOWITSCH (*J. Soc. Chem. Ind.*, 1894, **13**, 617—621).—The author has proved by a long series of experiments that the colour tests with sulphuric and phosphoric acids, phosphomolybdic acid, and chlorine gas are quite untrustworthy. The colours produced by these reagents are not due so much to the fat or oil as to some impurities generally occurring in them. As soon as these are removed by an improved manufacture, the tests no longer show the adulteration.

L. DE K.

The Correct Iodine Number. By HUGO SCHWEITZER and EMIL E. LUNGWITZ (*J. Soc. Chem. Ind.*, 1895, **14**, 130—133).—The authors have proved by a large number of experiments that when working with the Hübl solution the action is not merely an additive one, but that substitution, with formation of hydrogen iodide, also takes place. The true iodine number is therefore obtained by subtracting from the total iodine absorbed, the iodine corresponding with the liberated hydrogen iodide.

This is estimated, after the usual titration with potassium iodide and sodium thiosulphate, by adding some potassium iodate and again titrating the liberated iodine, the amount of which depends on the quantity of free acid in the mixture. A large proportion of the acid may, however, be due to the Hübl solution, and the usual blank experiment should therefore be made.

L. DE K.

Determination of the Oxidisability of Oils. By W. BISHOP (*J. Pharm.*, 1896, [6], **3**, 55—61).—The oxidation of oil is greatly facilitated by the addition of a little manganese resinate, which is obtained from the commercial product by extraction with light petroleum or ether. The oil (5—10 grams) is mixed with the resinate (2 per cent.) until the latter is completely dissolved, the solution (1·2 gram) is intimately mixed with calcined anhydrous precipitated silica (1 gram), and exposed to the air at 17—28°; in the case of non-drying oils, such as colza and olive oil, the best temperature is 20—30°. The assay is weighed at the end of 2, 6, and 16 hours, a fresh surface being exposed after each weighing. An oil of normal density but of poor quality is readily detected, and the values obtained serve to control, or even replace, the "iodine number," moreover, valuable information is obtained as regards the nature of the oil, its maximum degree of oxidation, and the time required to attain this.

The following numbers give the average maximum percentage increase of weight shown by the respective oils when treated as above; the density of each is given in brackets. Linseed oil (French) = 17·05 (0·9327); linseed oil (La Plata) = 15·20 (0·9304);

hemp seed oil = 14.40 (0.9287); poppy seed oil (French) = 14.20 (0.924); nut oil (commercial) = 13.70 (0.924); cotton seed oil (demargarified) = 9.45 (0.923); cotton seed oil = 8.60 (0.924); sesame oil (Senegal) = 8.70 (0.9215); sesame oil (Indian) = 7.40 (0.921); palm oil (African) = 6.70 (0.916); palm oil (white) = 6.50 (0.916); colza oil (French) = 6.40 ? (0.9142); colza oil (Indian) = 5.85 ? (0.9137); olive oil = 5.30 ? (0.9155). The oxidation of colza oil and olive oil proceeds so slowly that it is doubtful whether the above values are the maxima.

J. B. T.

Detection of Vegetable or Animal Oil in Mineral Oil. By GEORGES HALPHEN (*J. Pharm.*, 1896, [6], 3, 16—19).—Royère's test for animal and vegetable oil in mineral oil is based on the fact that the former contains acids, and therefore give a rose coloration when mixed with aqueous magenta solution which has been decolorised by means of soda. It is pointed out that mineral oil (petroleum) contains acids, even when prepared with the greatest care and in a high state of purity. A considerable number of lubricants are known, of variable consistency, composed of mineral oil intimately mixed with an alkali, or alkaline-earth-soap; in these cases also the test does not apply as the acids are neutralised. The presence of alkali in such substances is readily detected by agitation with a solution of Congo red which has been rendered violet by the minimum amount of hydrochloric acid.

J. B. T.

Commercial Analysis of Lard. By HUGO SCHWEITZER and EMIL E. LUNGWITZ (*J. Soc. Chem. Ind.*, 1894, 13, 614—616).—The authors state that it is easy to prepare a compound which will pass as pure lard, when judged by its specific gravity, melting point, saponification equivalent, refractive index, and volatile fatty acids.

Cotton seed oil and similar vegetable oils may be detected by Milliau's phosphomolybdic acid test or by his modified Bechi's silver test. Should these tests point to adulteration, the rise of temperature with sulphuric acid and the iodine absorption should be taken. The crystallisation point is also a good test for the purity of lard; to detect addition of tallow, the sample should be recrystallised from ether, and the deposit microscopically examined.

L. DE K.

Analysis of Lard Oil. By HUGO SCHWEITZER and EMIL E. LUNGWITZ (*J. Soc. Chem. Ind.*, 1895, 14, 129).—Any sample with a higher iodine number than 70 should not show any sign of cloudiness above 40° F.; oils with an iodine number of 60—64 are generally pasty at that temperature.

The congealing point is taken by putting the oil in a 4 oz. wide-mouth bottle surrounded by a mixture of ice and salt and stirring vigorously with a thermometer; when the oil shows the first sign of becoming cloudy, the temperature is recorded.

L. DE K.

Analysis of Whale Oil. By HUGO SCHWEITZER and EMIL E. LUNGWITZ (*J. Soc. Chem. Ind.*, 1895, 14, 130).—The authors having

examined a large number of samples of pure whale oil, state that the refined oil should have the following qualities. It must be clear and of a pale yellow colour; its specific gravity must be between 0.921 and 0.923 at 15.5°; the iodine number must be between 120 and 130.

The melting point of the fatty acids must not be higher than 20°, and the saponification value should be between 190 and 200. The Milliau test should leave the fatty acids unaffected. L. DE K.

Santal Wood Oil. By ERNEST J. PARRY (*Pharm. J. Trans.*, 1895, 55, 118—119).—Santal wood oil is digested with an equal volume of acetic acid in a pressure flask for an hour and a half at 150°, washed until free from acid, dried, and the oil then saponified with alcoholic potash, the amount of the latter used being noted; this in the case of the genuine oil is found to be equal to about 19 per cent. on the weight taken. Cedar wood oil, a common adulterant of the former, when similarly treated, only requires about 2 per cent. of potash. The author thinks the difference can be depended on to detect adulterations of 10 per cent. and upwards. R. R.

Analysis of Soap. By ED. SPAETH (*Zeit. angew. Chem.*, 1896, 5—9).—In order to avoid the use of a weighed filter and the troublesome removal of the insoluble matter from the sides of the beaker, the author now recommends drying and afterwards extracting with alcohol in the apparatus previously described by him for the testing of butter (*Abstr.*, 1894, ii, 124).

The moisture may also be estimated by drying the sample after mixing with sand, or by dissolving in proof spirit and evaporating an aliquot part of the solution. In presence of glycerol or other more or less volatile matter, the water cannot be estimated by a direct experiment. The total alkali is estimated by decomposing the alcoholic solution of the soap by a known amount of normal acid and agitating the liquid in a separating funnel with light petroleum; the alcoholic liquid is then drawn off, and the petroleum washed twice with a little proof spirit which must be added to the main liquid; the excess of acid is then titrated with normal alkali. An aliquot part of the light petroleum containing the fatty matter is distilled in a small, weighed flask, and the residue finally dried in a current of dry hydrogen. L. DE K.

New Reaction for the Detection of Soap in Lubricants. By HUGO SCHWEITZER and EMIL E. LUNGWITZ (*J. Soc. Chem. Ind.*, 1894, 13, 1178).—Five drops of the oil or melted fat is dissolved in 5 c.c. of benzene (boiling point below 75°) and 1 c.c. of a saturated solution of metaphosphoric acid in absolute alcohol is added. If the fats are free from soap, the mixture remains clear for even 24 hours, but in the presence of soap, or of so-called "gelatin" (which is mineral oil containing 10 per cent. of alumina soap) an immediate precipitate of a metallic phosphate is obtained. When testing waxes or ozokerite, the substance and the reagent should both be dissolved in ether.

If, on adding to the alcoholic ethereal solution containing the phosphatic precipitate, a drop of alcoholic platinum chloride, the

precipitate dissolves, a sodium, calcium, or magnesium soap is most likely present; a crystalline appearance in the precipitate indicates potassium, whilst if the precipitate remains unchanged, the presence of iron or aluminium soaps may be suspected. L. DE K.

Detection of Aloes in Mixtures. By ALOIS KREMEL (*J. Pharm.*, 1895, [6], 2, 503—505).—To remove foreign matters which would interfere with the tests for aloes, the tincture, or the alcoholic extract of solid material, or, in the case of an aqueous solution, the alcoholic extract of the residue left on drying, is concentrated on a water bath, extracted with hot water so as to make a 1 per cent. solution of aloes, treated with excess of basic lead acetate, filtered, and the excess of lead removed by sodium sulphate; after filtration, the solution is ready for tests for aloes with bromine, copper sulphate, ammonia, or nitric acid. D. A. L.

Identification of Alkaloids and Glucosides. By EMANUEL FORMÁNEK (*Chem. Centr.*, 1895, i, 1148; from *Pharm. Post*, 18, 179).—Aloin dissolves in nitric acid with a red coloration, changing to yellow; the residue after evaporation gives a red solution with alcohol, which changes to brown with gaseous ammonia, to yellow with soda, and to violet and rose successively, with alcoholic potassium cyanide. Amygdalin gives a yellow residue on evaporation with nitric acid; this changes to rose-red with gaseous ammonia, brownish-red with aqueous ammonia, and rose-violet with alcoholic potash. Brucine, after treatment with nitric acid, gives a yellow residue which becomes grass-green with aqueous ammonia, and violet with hydrogen sulphide solution. Cotoin gives a dull green coloration with nitric acid, the residue after evaporation being brownish-red; with gaseous or aqueous ammonia, it changes to dull green, and then to brown. Emodin yields a brownish-red residue with nitric acid, changing with aqueous ammonia to violet, then to dull red; with alkali, the colour is violet, changing to brown. Narcotine gives a yellowish-green residue with nitric acid, changing with gaseous ammonia to dull green, then to brown; the same colour is produced by alkali, but on heating it becomes brick-red. Physostigmin gives a cinnabar-coloured residue with nitric acid which becomes green when heated or dissolved in water; with alkali or ammonia, the green slowly changes to brown. With nitric acid, salicin gives a light yellow residue, which becomes blood-red when heated with potassium cyanide. Strychnine gives a yellow residue with nitric acid, changing to orange-yellow with ammonia; dilute alcoholic alkali colours this residue reddish-violet, then it slowly turns brown; the presence of brucine in considerable proportion has no effect on these reactions. J. B. T.

Estimation of Nicotine and Ammonia in Tobacco. By RICHARD KISSLING (*Zeit. anal. Chem.*, 1895, 34, 731—734).—The author is unable to acquiesce in either the objections to his process, or the modifications therein proposed by Vedrödi (see *Abstr.*, 1882, 1005; 1893, ii, 504; 1894, ii, 75; 1895, ii, 541). Light petroleum is

a less suitable solvent for the nicotine than ethylic ether, since it is never entirely free from high-boiling constituents, and these must interfere with any attempt to distil off the petroleum without loss of nicotine (which, however, Vědrödi does not propose to do). If the process is carried out according to the original instructions, there is no danger of soda being carried over with the nicotine. On the other hand, Vědrödi's test analyses were carried out with an entire disregard of his own caution (Abstr., 1893, ii, 504) that the amido-compounds in tobacco are decomposed with evolution of ammonia when heated with soda. The estimation of ammonia in tobacco is a far less simple matter than is assumed by Vědrödi. The following is the process given in the author's "Tabakkunde." The nicotine is first estimated. Then 10 grams of tobacco is extracted with 100 c.c. of 40 per cent. alcohol in a flask with reflux condenser, the extract filtered when cold, and an aliquot part of it freed from alcohol; the residue is then mixed with dilute sulphuric acid, and the albumin, peptones, nicotine, and ammonia are precipitated by the smallest possible excess of phosphomolybdic acid. An aliquot part of the filtrate from this precipitate is evaporated with some barium chloride, and the nitrogen it contains determined. A third portion (20 grams) of the tobacco is digested with about 350 grams of water acidified with sulphuric acid, the total solution (including the moisture of the original tobacco) made up to 400 grams, and 200 grams of the filtrate is freed from proteids by the addition of mercuric chloride. An aliquot part of the filtrate is freed from mercury by hydrogen sulphide, and the amides are converted into amido-acids and ammonia by boiling the acid filtrate for an hour. After the addition of an alkali, the ammonia and nicotine are distilled over into titrated sulphuric acid. These results give the data for calculating the ammonia, amides, and nicotine, and the remaining nitrogen in the tobacco is assigned to albumin.

Finally, attention is called to errors of calculation in Vědrödi's paper. M. J. S.

Estimation of small Amounts of Aniline in Toluidine, and of Toluidine in Aniline. By PAUL DOBRINER and WILHELM SCHRANZ (*Zeit. anal. Chem.*, 1895, **34**, 734—740).—Reinhardt has shown (*Chem. Zeit.*, **17**, 413) that the proportions of aniline and toluidine in a mixture of the two can be calculated from the amount of bromine absorbed when a hydrobromic acid solution of the bases is treated with a mixture of potassium bromide and bromate, obtained by dissolving bromine in potash, and boiling the solution until free from hypobromite, inasmuch as, by the action of nascent bromine, aniline is converted into a tribromo-derivative, whilst the toluidines yield only dibromo-derivatives. The formula $x = 2.37 vt - 1.37 a$, in which a is the weight of the mixture, v the volume of bromine solution, t its titre referred to pure aniline, gives x the amount of aniline present. Since the strength of the bromine solution is ascertained by experiments on pure aniline, the above formula is calculated on the supposition that 160.5 parts of toluidine will absorb exactly as much bromine as 93 parts of aniline, and for mixtures in which the aniline predominates, this assumption is sufficiently near the truth,

very small proportions (1 per cent.) of toluidine, added to pure aniline, being shown with considerable accuracy. But when the same formula is applied to mixtures in which toluidine is the chief constituent, the numbers for aniline come out somewhat too high, in consequence, it would seem, of the formation of small quantities of monobromotoluidine. In such cases, the error may be entirely obviated by standardising the bromine solution with pure toluidine, and calculating the titre for aniline by multiplication with $\frac{93}{160.5}$, or if t and T , the titres for aniline and toluidine respectively, be both ascertained experimentally, the equation becomes $V = \frac{x}{t} + \frac{a - x}{T}$ (erroneously given in the original as $\frac{x - a}{T}$). The end of the bromination is ascertained by iodised starch paper. With paratoluidine, the bromine solution must be added slowly. M. J. S.

Estimation of Water in Aniline and in Ortho- and Paratoluidine. By PAUL DOBRINER and WILHELM SCHRANZ (*Zeit. anal. Chem.*, **34**, 740—742).—By means of Reinhardt's process (see preceding abstract), the amount of water in aniline, or orthotoluidine, or any mixture of the two, may be very easily estimated. It suffices to ascertain the bromine absorption, a , of the sample in its original condition, and b , after drying with ignited potassium carbonate. The percentage of water is then equal to $100(b - a)/b$. Two treatments with potassium carbonate should be given, since a single treatment does not entirely remove the water.

This method does not succeed with paratoluidine, but, since commercial paratoluidine contains but little aniline, it suffices to distil off about 10 per cent., when the remainder may be regarded as dry. Other substances which exhibit a constant bromine absorption may be similarly examined, and the authors are endeavouring to apply the method to substances which do not absorb bromine, by adding a known amount of dry aniline and then proceeding as above.

M. J. S.

Estimation of Morphine in Opium. By LYMAN F. KEBLER (*J. Soc. Chem. Ind.*, 1895, **14**, 464—466).—The morphine obtained in an opium assay is never quite pure, but leaves a small percentage of ash; merely deducting this ash, however, does not give the true amount of the alkaloid. The ash should be analysed, and its calcium carbonate calculated into calcium meconate, which, with the weight of the remainder of the ash, is deducted from the weight of the morphine precipitate. L. DE K.

Estimation of Tanning Matter. By HENRY R. PROCTER (*J. Soc. Chem. Ind.*, 1894, **13**, 494—495).—The gravimetric process, consisting in determining the total solids of a bark infusion before and after treatment with hide powder, the difference being taken as tannin, is still considered the best. The hide powder must, however, be

thoroughly washed to remove any soluble matter, and then well squeezed. In accurate analysis, it is necessary to allow for the number of cubic centimetres of water introduced into the mixture by the moisture of the hide powder, and this may be done with sufficient accuracy by strongly pressing a known weight of the damp powder in folds of cloth and noticing the diminution in weight.

If the mixture be agitated violently by means of machinery for 10 minutes with three successive portions of hide powder, the tannin will be found to have been completely removed. L. DE K.

A Colorimeter: Colorimetric Estimation of Hæmoglobin. By WILHELM ZANGEMEISTER (*Zeit. Biol.*, 1896, **33**, 72—84).—The principle of the apparatus is the following: It consists of two glass tubes, and opening, at right angles, into the end of each is a funnel. Within the glass tubes, slide glass tubes having the inner ends closed; these tubes can be pushed to and fro; if the glass is pulled out, the liquid in the funnel runs into the tube, and in this way liquid is drawn into the tube until the tint, seen lengthwise, equals that in the other tube, which is a standard. The apparatus is described with full details, and is stated to give better results than the instruments of Gowers, Fleischl, &c. The results were controlled by estimations of iron in the ash. The same instrument may be used for the colorimetric estimation of other substances. W. D. H.

General and Physical Chemistry.

Wave-length of the D₃ Helium Line. By A. DE FOREST PALMER, jun. (*Amer. J. Sci.*, 1895, [3], 50, 357—358).—Owing to the recent increased interest in the wave-length of the helium lines the author has been led to calculate some observations which he has carried out on the D₃ chromosphere line. The measurements were made on a large, fixed telescope spectrometer, with a plane speculum metal grating, having about 14,000 lines to the inch, and 5 inches of grating space. The average of 17 values found gives 5878.939 ± 0.006 for the wave-length of the D₃ line. H. C.

Three different Spectra of Argon. By JOSEF M. EDER and E. VALENTA (*Monatsh.*, 1896, 17, 50—56).—The authors give a table of the wave-lengths from $\lambda = 2050$ to $\lambda = 2439$ of the lines in the blue argon spectrum. They find, also, that in addition to the blue and red spectra, there is a third spectrum of argon which is obtained by the application of very large condensers with a large Ruhmkorff and powerful currents in the primary coil. Under a pressure of 15 to 20 mm., a brilliant white light then appears in the capillary. Under pressures of 2 to 10 mm. the third spectrum is distinguished by the fact that many of the lines peculiar to the blue argon spectrum appear more distinct, and others weaker, and that entirely fresh lines become visible. The red argon spectrum disappears completely in low pressure tubes, but appears again partially when the pressure is increased. At 20 mm. pressure, many of the lines completely coincide with those of the red and blue spectra, but whole groups of lines show a displacement towards the red end of the spectrum, although the connection between these and corresponding lines of the blue spectrum is apparent.

The authors are unable to confirm Crooke's statement that the red argon spectrum is produced by the positive, and the blue spectrum by the negative pole. H. C.

Electrolytic Dissociation and Light Absorption. By FREDERICK G. DONNAN (*Zeit. physikal. Chem.*, 1896, 19, 465—488).—The author has investigated the light absorption of solutions of violuric acid by aid of a colorimeter, of which diagrams and a description are given. The dissociation in N/32, N/64, N/128, and N/256 solutions are calculated from the absorption, and the results are found to agree well with those obtained from the conductivity. The addition of hydrogen chloride causes a decrease in the dissociation, and the concordance of the colorimetric and conductivity results is again satisfactory. Para-hydroxybenzoic acid was also employed instead of hydrogen chloride owing to the approximate equality of its dissociation constant to that of violuric acid, and in this case, as also for the addition of levulinic and acetic acids, satisfactory results for the decrease in dissociation were obtained colorimetrically. The addition of sodium chloride

gives rise to an indeterminate equation for the concentration of the colouring ions; but, on the assumption that the undissociated sodium violurate possesses an absorptive power equal to that of the acid ion, an approximate result is obtained which is, however, not in good agreement with the colorimetric observations. The assumption is afterwards shown to be not quite correct, as the absorptive power of the salt is slightly greater than that of the acid ion. (See also Abstr., 1893, ii, 510; 1894, ii, 8, 226; 1895, ii, 433.) L. M. J.

Phosphorescent Radiations. By HENRI BECQUEREL (*Compt. rend.*, 1896, 122, 420—421).—When potassium uranium sulphate is placed on a sheet of paper, which is laid on a gelatino-bromide plate previously wrapped in two sheets of thick, black paper, and exposed to sunlight for several hours, a black silhouette of the phosphorescent substance is obtained on the plate on development. When pieces of money or metal screens are interposed between the phosphorescent substance and the photographic plate, an image of these objects is obtained on development. The same results are obtained when a thin sheet of glass is placed between the uranium salt and the paper, and hence they cannot be attributed to the action of vapours given off by the phosphorescent substance. C. H. B.

Absorption of Röntgen Rays by Chemical Compounds. By V. NOVÁK and OTTOKAR ŠULC (*Zeit. physikal. Chem.*, 1896, 19, 489—492).—The authors have determined qualitatively the transparency to the Röntgen rays of various chemical compounds. Compounds containing only carbon, hydrogen, oxygen, and nitrogen are, as a rule, transparent, but opacity is induced by the presence of a halogen, the action of bromine and iodine being more marked than that of chlorine. The elements of low atomic weight fall into the following series. Sulphur = phosphorus, aluminium, magnesium, boron = carbon, the transparency increasing with decreasing atomic weight. Salts of like nature gave the following orders: rubidium, potassium, sodium, lithium, ammonium; barium, strontium, calcium, magnesium, beryllium; while, further, calcium and strontium possess absorptive powers approximately equal to those of potassium and rubidium. The acid radicles fall into the following series of increasing transparency: carbonate, nitrate, sulphate, chloride, bromide, iodide, chlorate, bromate, iodate, phosphate, arsenate. From this it appears that the absorptive power is a direct function of the atomic weight, or, in the case of radicles, of the mean atomic weight; while also for electrolytes the absorptive power is an additive function of the absorptive powers of the ions. L. M. J.

Colour Photography. Substitution of Organic Colouring Matters for the reduced Silver of Photographic Proofs. By GEORGES A. RICHARD (*Compt. rend.*, 1896, 122, 609—611).—Three negatives are taken, after the method of Ducos du Hauron, corresponding respectively with the red, blue, and yellow radiations of reflections of the subject; prints of each are then taken on sensitive plates or films, the result being three transparent positives giving in black the relative intensities of the red, the yellow, and the blue of

the original subject. The reduced silver forming these images is next converted into some compound capable of fixing or precipitating a red organic colouring matter for the first, a yellow for the second, and a blue for the third. The superposition of the three images gives a transparent, coloured reproduction of the subject. No information is given respecting the modes of treatment or the colouring matters best adapted to the purpose. J. F. T.

Parasite Electrodes. By G. DELVALEZ (*Compt. rend.*, 1895, **121**, 492—494).—When a strip of brass is placed between two copper electrodes in a rectangular vessel containing a solution of the mixed acetates of copper and lead, metallic deposits form on the side nearest to the positive electrode, and on the opposite side peroxide of lead is thrown down. The colours which these deposits present vary with the different conditions of electrolysis, and are described by the author. H. C.

Temperature of the Sparks produced by Uranium. By GABRIEL CHESNEAU (*Compt. rend.*, 1896, **122**, 471—473).—The sparks detached from uranium by friction with hard steel, &c., instantly ignite mixtures of methane and air, and it follows, from the results of Mallard and Le Chatelier, that their temperature cannot be below 1000°. They also ignite alcohol, benzene, or light petroleum which has been poured on cotton. Sparks detached from steel by means of flint ignite none of these gases and vapours. C. H. B.

Optical Method of Determining the Critical Temperature. By MICHAEL ALTSCHUL (*Chem. Zeit.*, 1895, **19**, 1917—1918).—In the optical method of determining the critical temperature, the point at which the meniscus of the liquid disappears and that at which it reappears are observed. It has been asserted by some observers that these two points do not coincide, and as, if this were the case, uncertainty would be introduced into determinations of the critical temperature by this method, the author has submitted this point to direct examination by experiment. He finds that there is no difference between the temperature at which the meniscus disappears and that at which it reappears. Where differences have been assigned, this was probably due to the liquid not having fully acquired the temperature of its surroundings. Even in the case of mixtures of liquids, the two temperatures are absolutely coincident. H. C.

Some Physical Aspects of Argon. The Ideal Thermometrical Substance for High Temperatures. By W. R. QUINAN (*J. Amer. Chem. Soc.*, 1895, **17**, 477—483).—Argon has dispelled certain beliefs in regard to monatomic gases. High boiling points can no longer be regarded as characteristic. Diatomic gases, such as hydrogen and nitrogen, have a fatal theoretical defect when used as thermometrical substances at very high temperatures; being diatomic, a certain part of their energy takes the form of internal energy; a part of the heat being thus latent, and being without effect on the temperature, equal quantities of heat cease to correspond with equal degrees of temperature. Argon has no internal energy; the decom-

posing influence of heat is absent; being monatomic, it cannot suffer dissociation, and its behaviour as a thermometric substance throughout the range of temperature will be strictly normal. Therefore at high temperatures argon is the ideal thermometric substance.

H. C.

Vapour Tensions of Mixtures of Volatile Liquids. By CHARLES E. LINEBARGER (*J. Amer. Chem. Soc.*, 1895, **17**, 615—652, and 690—718).—Up to the present, investigations of the vapour tensions of mixtures of liquids have been mainly confined to cases in which the dissolved substance is supposed to be non-volatile, and the solutions are made dilute. In the few cases in which mixtures of two volatile liquids have been considered, it has been usual to work with such as are now known to be composed of associated molecules, and to make no attempt to determine the partial pressure exerted by each vapour. The author has therefore determined the vapour tensions of mixtures in all proportions of certain "normal" liquids which are freely soluble in one another, and has further determined the partial pressures of the mixture's components, and also their concentrations in the gaseous phase.

The method used was founded on the determination of the quantity of a volatile liquid carried off by a definite volume of an inert gas made to pass through it, and the direct subsequent analysis of the gaseous mixture, either by passing it through appropriate liquid absorbents, or over decomposing agents. A full description of the apparatus used is given in the paper. The method can be said to give the vapour tensions of pure liquids with an accuracy equal to that obtainable by the best of other methods only when the liquids are not very volatile, but the results obtained by it for mixtures of liquids of not too different volatilities are accurate enough to serve as the experimental basis for theoretical deductions and generalisations.

The tension of the mixed vapour emitted by the mixtures of the volatile liquids examined was always greater than the tension of the less volatile liquid, and always less than that of the more volatile liquid; also the partial pressure of either component of any mixture was always less than the vapour tension of the component in a state of purity. The mixtures examined may be divided into four classes. The first class, represented by mixtures of benzene and toluene with monochloro- and monobromo-benzene, present the very simplest phenomena, the vapour tensions of these mixtures being linear functions of the concentration. The second class is represented by mixtures of chloroform with benzene and with toluene, and here the vapour tension is less than that resulting from the calculation by the rule of mixtures, the variation reaching a maximum when 100 molecules of the mixture contain from 50 to 60 molecules of chloroform. In the third class, of which mixtures of carbon tetrachloride with toluene and with benzene are representative, a very different behaviour was noticed. When benzene or toluene is added to carbon tetrachloride, the curve of total tensions follows closely the line connecting the points corresponding with the vapour tensions of the mixed liquids, until towards the abscissæ value of 80; the curve then commences to fall, only to rise again, and pass above the straight line, when finally

it changes its direction to fall upon the axis of ordinates at the point corresponding with the vapour tension of the pure hydrocarbon. The curve has, therefore, three turning points. The fourth class of mixtures, of which the only representative here was a mixture of nitrobenzene and carbon tetrachloride, is really that of a volatile liquid with an almost non-volatile one. As would naturally be expected, the partial pressure of the carbon tetrachloride and the total pressure of the mixture are almost identical.

It was found by direct experiment that the laws deduced from observations made at any one temperature are applicable to any other temperature, at any rate when the latter is not very far removed from that of the observations. The relations between the concentrations in the gaseous and liquid phases were found to be quite simple, and entirely in accordance with the provisions of the theoretical relations established by Planck and Nernst.

The vapour tensions of mixtures of acetic acid with benzene and with toluene were determined, and from the results the author calculates the molecular mass of the dissolved and liquid acid, the numbers agreeing with those obtained by Ramsay and Shields. A general method for the determination of the molecular masses of associated liquids at any given temperature is indicated in these results.

H. C.

Thermochemistry of Chlorobenzoic acid and some of its Derivatives. By PAUL RIVALS (*Compt. rend.*, 1896, **122**, 480—482).

—*Orthochlorobenzoic acid*: Heat of combustion per gram +4688 Cal. per molecule +773·7 Cal.; heat of formation +103·0 Cal.; heat of neutralisation +15·5 Cal., which is 1·5 Cal. higher than that of benzoic acid.

Potassium chlorobenzoate, $2C_7H_4ClO_2K + H_2O$: Heat of dissolution +0·72 Cal.

$C_7H_4ClO_2K$ diss. + HCl diss. = $C_7H_5ClO_2$	
pptd. + KCl diss.	develops +4·4 Cal.
$C_7H_5ClO_2$ sol. + Aq = $C_7H_5ClO_2$ diss.	absorbs -6·2 „
$C_7H_5ClO_2$ sol. + KOH sol. = $(C_7H_4ClO_2K$	
+ $\frac{1}{2}H_2O$) sol. + $\frac{1}{2}H_2O$	develops +21·2 „

Chlorobenzoic chloride: Heat of combustion per molecule +743 Cal.; heat of formation (liquid) +64 Cal., and hence

$C_7H_4ClO_2$ liq. + H_2O liq. = $C_7H_5ClO_2$ sol.	
+ HCl gas	develops -7·2 Cal.

Whereas in aldehyde practically the same amount of heat is developed by the substitution of chlorine for either the functional hydrogen or the hydrogen of the methyl group; in benzaldehyde, on the other hand, the substitution of chlorine in the nucleus is comparable with its substitution in the methyl radicle, but the contiguity of the nucleus modifies the character of the aldehyde group, and the substitution of chlorine for the functional hydrogen results in a development of heat of a very different order of magnitude.

C. H. B.

Thermochemistry of the Amides and Ammonium Salts of some Chloro-acids. By PAUL RIVALS (*Compt. rend.*, 1896, **122**, 617—619).

Heats of neutralisation:—

$\text{CH}_2\text{Cl}\cdot\text{COOH}$ diss. + NH_3 diss.	+12.7 Cal.
$\text{CCl}_3\cdot\text{COOH}$ diss. + NH_3 diss.	+13.1 "
$\text{C}_6\text{H}_5\cdot\text{COOH}$ diss. + NH_3 diss.	+12.1 "
$\text{C}_6\text{H}_4\text{Cl}\cdot\text{COOH}$ (ortho) diss. + NH_3 diss..	+13.1 "

Heat of Formation of Chloro-amides.—The combustion is accelerated by adding a known weight of camphor. The following are the figures.

1 gram $\text{CH}_2\text{Cl}\cdot\text{CO}\cdot\text{NH}_2$ develops on burning..	+2599 Cal.
1 " $\text{CCl}_3\cdot\text{CO}\cdot\text{NH}_2$ " " ..	+1020 "
1 " $\text{C}_6\text{H}_4\text{Cl}\cdot\text{CO}\cdot\text{NH}_2$ " " ..	+5200 "

From these figures, the heats of combustion and of formation are deduced.

	Heat of combustion.		Heat of formation. Cal.
	at const. vol.	at const. press.	
$\text{CH}_2\text{Cl}\cdot\text{CO}\cdot\text{NH}_2$	+243.0 cal.	+242.9	+88.6
$\text{CCl}_3\cdot\text{CO}\cdot\text{NH}_2$	+165.9 "	+165.2	+107.1
$\text{C}_6\text{H}_4\text{Cl}\cdot\text{CO}\cdot\text{NH}_2$	+808.9 "	+808.2	+63.5

Determination of the heat developed in the formation of chloro-amides from ammonia and the chloro-acid gave the following figures.

$\text{CH}_2\text{Cl}\cdot\text{COOH}$ sol. + NH_3 gas = $\text{CH}_2\text{Cl}\cdot\text{CO}\cdot\text{NH}_2$ sol. + H_2O liq.	19.5 Cal.
$\text{CCl}_3\cdot\text{COOH}$ sol. + NH_3 gas = $\text{CCl}_3\cdot\text{CO}\cdot\text{NH}_2$ sol. + H_2O liq.	19.2 "
$\text{C}_6\text{H}_4\text{Cl}\cdot\text{COOH}$ sol. + NH_3 gas = $\text{C}_6\text{H}_4\text{Cl}\cdot\text{CO}\cdot\text{NH}_2$ sol. + H_2O liq.	17.2 "
	J. F. T.

Heats of Solution of some Carbon Compounds. By CLARENCE L. SPEYERS (*J. Amer. Chem. Soc.*, 1896, **18**, 146—156).—The heats of solution of some solid carbon compounds in water, methylic, ethylic, and propylic alcohols, chloroform, and toluene were determined by means of the simple method given by Nernst. The quantity of solvent compared with the quantity of substances dissolved was always so large that it is safe to conclude that further addition of solvent would produce no appreciable development of heat. The following table shows the heats of solution in a convenient form for comparison.

The solvents with which the numbers in each of the columns were obtained were: I, water; II, methylic alcohol; III, ethylic alcohol; IV, propylic alcohol; V, chloroform; VI, toluene. The numbers give the heats of solution in small calories.

	I.	II.	III.	IV.	V.	VI.
Urea	-3628	—	-3612	—	—	—
Urethane	-3787	-4345	-4728	-6045	-4573	-6399
Chloral hydrate.....	-929	—	-1131	—	-5993	-7537
Succinimide	-4294	—	-5456	—	—	—
Acetamide	-1991	—	-3606	—	—	—
Mannitol.....	-5262	—	—	—	—	—
Resorcinol	-3960	—	+ 269·2	—	—	—
Benzamide	—	—	-4238	—	—	—
Paratoluidine.....	—	—	-3650	—	-3492	-4983
Acetanilide	—	-4477	-4212	—	-4442	—
Acenaphthene	—	-6180	-5986	-6807	-4480	-4788
Naphthalene	—	-4233	-4861	-5681	-3852	-4267
Phenanthrene	—	—	-4306	—	—	-3528
Cane sugar	-1318	—	—	—	—	—

H. C.

Molecular-volumetric Method of Determining the Molecular Weight. III. By ISIDOR TRAUBE (*Ber.*, 1896, 29, 1023—1029; compare *Abstr.*, this vol., 235).—The author has calculated the co-volumes of a large number of substances by subtracting the sum of the atom-volumes of the constituent elements from the molecular volume obtained by dividing the molecular weight by the density, the proper allowance being made for the various types of rings, &c., present in the molecule. The atom-volumes employed are those which have been deduced from the study of the density of aqueous solutions of compounds of these elements, except in the cases of bromine and iodine, for which the values 17·7 and 21·4 respectively have been adopted. The molecular co-volume is thus found, for the great majority of substances, to be approximately constant, and equal to 25·9 c.c. at 15°. For substances which tend to form associated molecules, especially such as contain methyl and hydroxyl, the molecular co-volume is smaller than the average, and falls, as a rule, between 15 and 22. For tertiary substances, such as amines, compounds containing several halogen atoms, and ethers of high molecular weight, the molecular co-volume, on the other hand, is greater than the average, and generally falls between 30 and 32. In the cases of a few tertiary amines it is still higher. The density method can therefore be used for the determination of the molecular weight of liquids and solids, if sufficient information as to the valency of the nitrogen atoms, the mode of combination of the oxygen atoms, the types of ring present, &c., is available. If it is not, the molecular weight may be independently ascertained, and the density employed for the determination of the constitution.

A. H.

Cryoscopic Investigations. By A. PONSOT (*Compt. rend.*, 1896, 122, 668—670).—The author has determined the limiting value of the molecular reductions of the freezing point of various solutions by the method already described (*Abstr.*, 1894, ii, 342), and has obtained the following results.

Cane sugar	18·77	Potassium bromide ..	34·82
Acetic acid	18·5	Barium chloride	50·5
Oxalic acid	33·95	Calcium chloride	51·8
		Lead nitrate	47·0
Sodium chloride	34·28	Potassium sulphate ..	48·45
Potassium chloride...	34·16	Sulphuric acid	47·20

Carbon compounds have not all a molecular reduction approximating to 18·5, and metallic salts of the same type have not exactly the same molecular value, contrary to the hypothesis of Arrhenius. If curves of molecular reduction are plotted, by taking the actual reductions as abscissæ and the molecular reductions as ordinates, the curves for potassium chloride, potassium bromide, and acetic acid have the same form as that for sodium chloride, and cut the axis of the ordinates almost perpendicularly, so that in very dilute solutions the reduction of the freezing point is practically proportional to the weight of salt in 100 grams of the solution. This result can be deduced from van't Hoff's equation if the variation in the concentration of the solution with the height of the liquid column is negligible (Abstr., 1895, ii, 206). Consideration of the behaviour of sugar solutions, assuming that the sugar is distributed in the column of liquid as if it alone occupied the column, and was in the state of a perfect gas, shows that the experimental results agree closely with the mathematical expressions, and leads to the conclusion that when a sugar solution is placed in an osmotic tube, the lower part of which is immersed in pure water, the osmotic pressure is equal to gaseous pressure only at the level of the pure water.

The curves for oxalic acid, lead nitrate, and potassium sulphate indicate that the molecular reduction decreases as the concentration increases up to the formation of cryo-salts (Abstr., 1895, ii, 438). The curves for barium chloride, calcium chloride, and sulphuric acid show that in these cases the molecular reduction at first decreases very rapidly as the concentration increases, reaches a minimum, and then increases again. The solutions of both these groups of compounds have a heat of dilution which is not negligible even in dilute solutions, and if van't Hoff's equation is applied to them, i must be regarded not as a constant, but as a quantity which varies with the concentration. C. H. B.

Determinations of the Molecular Weights of Some Inorganic Compounds. By HEINRICH BILTZ (*Zeit. physikal. Chem.*, 1896, 19, 385—430).—This is a more complete account of the author's experiments (this vol., ii, 152); details of the method, and illustrations of the apparatus employed, being given. L. M. J.

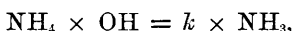
Affinity Constants of some Organic acids. By JOHAN M. LOVÉN (*Zeit. physikal. Chem.*, 1896, 19, 456—464).—The paper contains an extension of the author's determinations of the affinity constants of sulpho-derivatives of organic acids (Abstr., 1894, i, 325). The results obtained are given in the following table.

Acid.	<i>k</i> .
β -thiophencarboxylic acid	0·0078
Benzenesulphoneglycocine, $C_6H_5 \cdot SO_2 \cdot NH \cdot CH_2 \cdot COOH$	0·0351
Orthotoluenesulphoneglycocine	0·0282
Paratoluenesulphoneglycocine	0·0347
1 : 3 : 4-xylenesulphoneglycocine	0·0270
Pseudocumenesulphoneglycocine	0·0248
1 : 3 : 4-xylenesulphonealanine, $C_6H_5 \cdot SO_2 \cdot NH \cdot C_2H_4 \cdot COOH$	0·0243
Benzenesulphoneasparagine, $C_6H_5 \cdot SO_2 \cdot NH \cdot C_2H_3(COOH)_2$	0·0715
β -dibromomethanesulphonopropionic acid, $CHBr_2 \cdot SO_2 \cdot C_2H_4 \cdot COOH$..	0·0205
β -dichloromethanesulphonopropionic acid, $CHCl_2 \cdot SO_2 \cdot C_2H_4 \cdot COOH$..	0·0198
Benzenesulphinic acid (about)	3·5000
<i>p</i> -toluenesulphinic acid (about)	2·5000
Diphenyleneglycollic acid, $C_{10}H_8 \cdot C(OH) \cdot COOH$	0·1000
Selenodiacetic acid, $Se(CH_2 \cdot COOH)_2$	0·0424

The last value is slightly smaller than that of the corresponding sulpho-compound (*loc. cit.*). L. M. J.

Chemical Equilibrium in Ammoniacal Solutions of Magnesium Salts. By JOHAN M. LOVÉN (*Zeit. anorg. Chem.*, 1896, **11**, 404—415).—The fact that magnesium hydroxide is not precipitated by ammonia in the presence of ammonium salts has been explained by assuming that double ammonium and magnesium salts were formed in the solution, or else by assuming the formation of complex salts in which the magnesium formed part of the negative ion. Neither of these assumptions is satisfactory, and it appears more probable that, in accordance with the dissociation theory, the part played by the ammonium salt is that of diminishing the amount of dissociated ammonium hydroxide in the solution. The number of hydroxyl ions present being thus reduced, the tendency for the formation of magnesium hydroxide is considerably lessened.

For the equilibrium of ammonia towards ammonium and hydroxyl, we have the equation



where *k* is the dissociation constant of the ammonia. If *C* is the concentration of magnesium hydroxide in a saturated solution, and the magnesium hydroxide is fully dissociated, *C* is the concentration of the magnesium and 2*C* that of the hydroxyl ions. For the equilibrium of magnesium hydroxide toward the solution we have then



Combining this with the previous equation we get, finally,

$$C = \sqrt[3]{Mg \times \left(\frac{NH_3 \times k}{2 \times NH_4} \right)^2}.$$

The author has verified this relationship between the concentrations of the ammonia, the ammonium salts, and magnesium salts in solution. H. C.

The Velocity of Hydrolysis in Organic Solvents. By G. GENNARI (*Zeit. physikal. Chem.*, 1896, **19**, 436—440).—The velocities of hydrolysis were determined for methylic and ethylic acetates, in

methylic and ethylic alcohol solutions, sodium hydroxide and sodium ethoxide being employed. In ethylic alcohol, concordant results were obtained for the reaction constant, which was about 1/180 of the constant in aqueous solution, and smaller for the ethoxide than for the hydroxide. In methylic alcohol, however, the reaction does not proceed as rapidly, and soon ceases, notwithstanding the fact that the compounds are more strongly dissociated in this solvent. This result does not appear to be due to a reverse reaction, for experiments with sodium acetate and methylic alcohol gave no trace of alkali, so that dissociation does not appear to be the only factor affecting the velocity of hydrolysis.

L. M. J.

Inversion of Sugar by Salts. By JOHN H. LONG (*J. Amer. Chem. Soc.*, 1896, 18, 120—130).—The specific rotation of solutions of cane sugar is known to be decreased by the presence of many neutral salts, the diminution depending in varying degree on the molecular weights of the salts, the temperature, and the exposure to light. It was found, on examination of the syrup of ferrous iodide of the pharmacopeia, that an old solution was strongly levorotatory, while a fresh solution gave a very marked right-handed rotation. Portions of the syrup were placed in stoppered bottles, exposed to light, and polarised at intervals of some weeks, a steady diminution in the rotation, and finally a complete inversion, being observed. Later experiments with two portions of the same solution, one in a bottle only partially filled, showed that the presence of air increases the rapidity of inversion in a marked degree. A temporary change in temperature does not produce a permanent change in the rotation. The influence of heat only becomes marked at a temperature above 60°, and at 100° an inversion can be accomplished in two hours, which would require a period of some months at the ordinary temperature. It was further found that the rate of inversion is more rapid in bottles exposed to the light than in similarly filled bottles kept in the dark. The rapidity of inversion is further increased if the solution is exposed to the action of light and heat together.

A number of other ferrous salts, and also salts of manganese, zinc, aluminium, lead, cadmium, and mercury were examined in their behaviour towards sugar, and found to act like ferrous iodide. The salts tested, although commonly called neutral, are those in which the base is very weak when compared with the acid. By direct experiment, it was shown that in the case of ferrous iodide the inversion proceeds according to the law of Wilhelmy. The cause of the inversion of strong sugar solutions by these salts is to be found in their condition of partial hydrolysis by the solvent.

H. C.

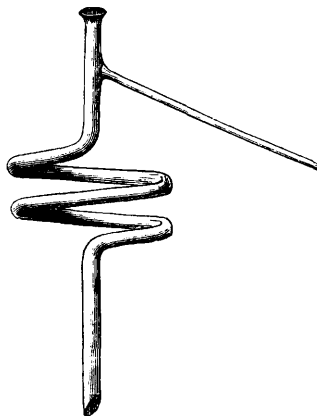
Reciprocal Salt Pairs. By WILHELM MEYERHOFFER (*Monatsh.*, 1896, 17, 13—28).—Pairs of salts which can be formed by double decomposition one from the other, such as KCl, NaBr, and KBr, NaCl, may be termed reciprocal salt pairs. At any given temperature one of the pairs will be stable and the other labile, so that the second pair will tend to become gradually converted into the first. Only at some one definite temperature would all four salts tend to

coexist in an unchanged condition. This point is, in the case of solutions of the salts, a sextuple point in the sense of the phase rule, as six phases here co-exist, the four salts, the solution, and aqueous vapour. Six equilibrium curves must therefore meet in this point, each curve being that for the equilibrium between five phases. The author has not as yet succeeded in obtaining the sextuple point in any special case, but he gives in this paper the results of his investigations with the salt pair, $\text{NaNO}_3 + \text{NH}_4\text{Cl}$. H. C.

Water of Crystallisation. By THEODOR SALZER (*Zeit. physikal. Chem.*, 1896, 19, 441—455).—The author adds the following rules regarding the water of crystallisation in hydrated salts to those previously enunciated (*Abstr.*, 1895, ii, 488). (1) The crystalline salts of those benzene derivatives in which two negative groups are present in the ortho-position, contain less combined water than the corresponding para-derivatives. (2) The number of water molecules in neutral bivalent metallic salts of dibasic organic acids, increases with the separation of the carboxyl groups. (3) The water content of calcium salts of organic acids containing a methyl group is not altered by the replacement of the latter by another normal alkyl group. A large number of examples are adduced in the paper in support of these rules. L. M. J.

A New Bunsen Burner. By R. DIERBACH (*Ber.*, 1896, 29, 865).—The burner described differs from the ordinary form in having an adjustable tube so attached to the foot that the flame can be placed in any required position. A. H.

A New Fractionating Column. By G. BERLEMONT (*Bull. Soc. Chim.*, 1895, [3], 13, 674—675).—This column, suggested by Lebel, consists of a glass spiral, as shown in the figure; it combines a large cooling surface with economy in height. A column of this kind only 36 cm. high is equal in efficiency to one of the old pattern containing six bulbs. It, moreover, enables the thermometer to be read more easily. J. F. T.



Modification of von Babo's Water-mercury Pump for the Production of High Vacua. By J. PRECHT (*Ber.*, 1896, 29, 1143—1145).—A modification of the von

Babo pump described by Krafft and Dyes (this vol., ii, 89). The chief changes consist in substituting ground or fused glass joints for the rubber connections, and a simple stopcock for the three-way tap. The rubber joints on the tubes through which the mercury falls and rises are conveniently retained, as they do not affect the efficiency of

the pump. A tube of phosphoric anhydride serves to absorb aqueous vapour. The glass joints are smeared with a mixture of wax and paraffin oil, as described by Hittorf, but lanolin may be used for the stopcocks. After working for two minutes, the pressure in the pump is unmeasurable by an ordinary manometer, a vessel of 1 litre capacity is exhausted to the same extent after 30 minutes, whilst after two hours the pressure in the pump = 0.00071 mm.; it is therefore well adapted for the preparation of tubes for the Röntgen rays.

J. B. T.

Inorganic Chemistry.

Conditions which regulate the Combination of Gases. Union of Oxygen and Hydrogen at Low Temperatures. By (E. J.) ARMAND GAUTIER and H. HÉLIER (*Compt. rend.*, 1896, **122**, 566—573).—The mixture of the dried gases is allowed to circulate through a porcelain tube, filled with small pieces of broken porcelain, for a known time, the quantity of water formed being determined by absorption, and weighing.

The temperature of the interior of the tube is determined by means of a pyrometer capable of giving readings within 2° .

By these means, the authors have arrived at the conclusion that the union of oxygen with hydrogen begins at a temperature of 180° , and can be determined at 200° . Between 300 — 310° , the combination is about 3·8 per cent. The following table gives the quantity of water formed between these temperatures.

Temp. of experiment.	Weight of gas passed.	Weight of water.	Prop. per 1000 of mixture.	Time in seconds.
304°	10·4262	0·0153	1·4	1·9
288	7·8216	0·0143	1·8	2·9
302	22·0365	0·0999	4·04	3·77
310	2·9445	0·0319	10·8	11·4
310	2·1365	0·0239	11·2	12·7
310	2·4989	0·0957	38·0	17·2
310	1·6264	0·0587	36·0	30·0
312	1·8322	0·0718	39·2	40·3
305	0·8473	0·0330	38·9	89·5
298	0·6731	0·0249	37·0	187·4

An attempt made to obtain the same results with the apparatus formerly employed by the authors, and lately used by V. Meyer and van't Hoff (in which the mixture is heated in closed tubes, and the contraction ascertained), gave no constant results. The water formed was in each experiment found to be alkaline, action on the glass evidently having taken place.

J. F. T.

Dimorphism of Ice. By H. P. BARENDRECHT (*Zeit. anorg. Chem.*, 1896, **11**, 454—455).—Solutions of water in methylic, ethylic, propylic, isopropylic, butyric or allylic alcohol, ether, glycerol, ethylene glycol, and lactic acid when cooled to a low temperature by means of solid carbonic anhydride, yield crystals which are very similar to the well known snow crystals. In mixtures of water with ethylic, propylic, isopropylic or allylic alcohol, besides the hexagonal crystals, large regular crystal skeletons are formed. The two crystal forms could not be separated. From a 60 per cent. solution of acetaldehyde, a crystalline mass which contained 37 per cent. of aldehyde was obtained by means of a centrifugal machine. A similar result was obtained by separating the hexagonal crystals from a 55 per cent. solution of alcohol in water. E. C. R.

An Oxidising Substance produced by distilling Aqueous Solutions of Potassium Permanganate and Sulphuric acid in a Vacuum. By COLIN C. FRYE (*Chem. News*, 1896, **73**, 122).—The author confirms the view generally entertained that when solutions of sulphuric acid and potassium permanganate are distilled in a vacuum, the distillate contains ozone. This does not occur if less than 22 per cent. of each reagent is present or if both solutions are above 50 per cent. in strength, for then large quantities of oxygen are evolved. D. A. L.

Action of some Hydrogen Compounds on Sulphuric Chloride. By ADOLPHE BESSON (*Compt. rend.*, 1896, **122**, 467—469).—Dry hydrogen sulphide acts on sulphuric chloride in the cold with production of hydrogen chloride, sulphurous anhydride, and sulphur, but some sulphur chloride is also formed in proportion which increases with the temperature, water being produced at the same time.

Dry hydrogen bromide at the ordinary temperature or on gently heating, decomposes sulphuric chloride with liberation of bromine and formation of hydrogen chloride and sulphurous anhydride. Hydrogen iodide behaves similarly, but some sulphur is liberated and water formed. Hydrogen phosphide yields hydrogen chloride, a crystalline, yellow phosphide, P_4S_3 , and red phosphorus, with phosphorous anhydride and traces of phosphoric chloride, $POCl_3$.

C. H. B.

Sulphur Nitride. By RUDOLF SCHENCK (*Annalen*, 1896, **290**, 171—185).—See this vol., i, 426.

Combination of Atmospheric and Chemical Nitrogen with Metals. By P. L. ASLANOGLU (*Chem. News*, 1896, **73**, 115—116).—The author has heated magnesium, copper, iron, zinc, and clay in the open air, and magnesium in purified atmospheric nitrogen and in ammonia, with the usual results. Aluminium gave a somewhat similar reaction to magnesium, but not distinctly enough to encourage further work with it. D. A. L.

Hyponitrous acid. By SIMEON M. TANATAR (*Ber.*, 1896, **29**, 1039).—Silver hyponitrite may be prepared, but only in small quantity, by

submitting a solution of barium acetate and sodium nitrite to electrolysis, and then acting with silver nitrate on an acetic acid solution of the crystalline barium hyponitrite which is formed. Hyponitrous acid is soluble in ether, and may be extracted from aqueous solution by means of this solvent. An ethereal solution of the acid, prepared by adding a solution of hydrogen chloride in ether to silver hyponitrite suspended in ether, left, on evaporation, a drop of a yellow, oily liquid which did not solidify at -19° , but when dissolved in water gave the characteristic reaction with silver nitrate. A. H.

Thiophosphites. By LUCIEN FERRAND (*Compt. rend.*, 1896, **122**, 621—622).—By heating a mixture of sulphur and red phosphorus, with different metals, a series of compounds of the general formula $PS_3M'_3$ is formed.

Copper thiophosphite, $(PS_3)_2Cu_3$, is made by heating molecular proportions of red phosphorus, copper, and sulphur to a red heat for 20 hours in a closed vessel. It forms crystals of a metallic lustre, red by transmitted light. It is fairly stable, but is decomposed by damp air.

Ferrous thiophosphite, $(PS_3)_2Fe_3$, a black substance crystallising in small plates. It is very stable.

Silver thiophosphite, PS_3Ag_3 , is obtained in the same way, it is a black, vitreous mass.

The author has also prepared the thiophosphites of chromium, zinc, and mercury.

Aluminiumthiophosphite, $(PS_3)_2Al_3$, [$?PS_3Al$], is a white solid, which is very unstable, and cannot be kept in the air. J. F. T.

Argon and Helium. By EDWIN A. HILL (*Amer. J. Sci.*, 1895, [3], **50**, 359—376).—The author replies to some criticisms of his former paper (this vol., ii, 16), and, more particularly, shows that there is little evidence in support of the assumption that argon, as a monatomic gas, can be compared to mercury vapour at 800° . Argon is analogous to the non-metals of low atomic weight and specific gravity rather than to the metals. Compounds are formed from argon on heating, and not on cooling, and the analogy with mercury therefore does not hold. The author thinks it probable that both argon and helium are mixtures. H. C.

Helium and Argon: Their Places among the Elements. By R. M. DEELEY (*Chem. News*, 1895, **72**, 297—298).—In a paper published in 1893 (*Trans.*, 1893, **63**, 852), the author showed that there was a blank for one element between hydrogen and lithium, and to this element gave an atomic weight of about 2.5. If helium has a diatomic molecule it would fill this place. The refraction equivalent of argon indicates that this gas is also diatomic, and places it between fluorine and sodium. H. C.

The Place of Helium and Argon in the System of the Elements. By W. PREYER (*Ber.*, 1896, **29**, 1040—1041).—The author points out that helium, with the atomic weight 4, argon, with the atomic weight 20, and the lighter constituent of the gas from

Clevéite, with the atomic weight of about 2, all find a place in the system of the elements proposed by him, and described in his work *Das genetische System der chemischen Elemente* (Berlin, 1893).

A. H.

The Formation of Sodium Carbonate in Nature. By SIMEON M. TANATAR (*Ber.*, 1896, **29**, 1034—1038).—When calcium carbonate is suspended in a solution of sodium sulphate, and the whole treated with a stream of carbonic anhydride and allowed to remain, sodium hydrogen carbonate is invariably formed. The amount produced is ascertained by filtering off the calcium sulphate and excess of calcium carbonate, boiling the clear liquid, filtering off the calcium carbonate thus deposited, and then titrating the solution with normal acid. The maximum amount of sodium hydrogen carbonate formed in this reaction, when 20 grams of sodium sulphate per litre are taken, is 2.9 grams per litre.

It is probable that sodium carbonate is actually formed in this way in nature, since it is always accompanied by sodium sulphate. Previous investigators have always made use of alcohol to remove the calcium sulphate produced, and have thus introduced an element of uncertainty into the matter.

The solubility of calcium hydrogen carbonate in water, which amounts to about 0.7 gram per litre, is greatly diminished by the addition of sodium hydrogen carbonate. When calcium carbonate is shaken up with a solution of sodium sulphate, the solution becomes alkaline, this being probably due to the increased solubility of the carbonate.

A. H.

Lithium Carbide. By HENRI MOISSAN (*Compt. rend.*, 1896, **122**, 362—363).—Lithium carbide, LiC_2 , is obtained as a transparent, white, crystalline mass of sp. gr. 1.65 at 18° , by heating 74 parts of lithium carbonate with 48 parts of sugar-carbon in the electric furnace at not too high a temperature. A current of 350 ampères and 50 volts suffices, and if heating is continued too long, part of the carbide is volatilised and decomposed.

Lithium carbide is a powerful reducing agent; it burns in fluorine and chlorine in the cold, in bromine and iodine vapours on gently heating, in oxygen and in sulphur and selenium vapours below dull redness, and in phosphorus and arsenic vapours at a red heat. Solid oxidising agents when fused attack it with great energy, but concentrated acids have very little action. Water decomposes the carbide in the cold with production of pure acetylene, and the decomposition becomes violent at about 100° .

C. H. B.

Action of Magnesium on Metallic and other Solutions. By DIOSCORIDE VITALI (*L'Orosi*, 1895, **18**, 289—303).—When metallic magnesium acts on aqueous ammonium chloride solution there is an abundant evolution of hydrogen; the metal dissolves, and ammonia is liberated. The older explanation of these facts, that is, that action occurs directly between the metal and the ammonium chloride, seems to be untrue; in all probability the magnesium first acts on the water, with liberation of hydrogen and formation

of magnesium hydroxide, and the latter then decomposes the ammonium chloride with liberation of ammonia. The action of magnesium on hydroxylamine hydrochloride supports this view, for hydrogen is liberated in abundance and hydroxylamine remains in solution; similarly mercuric cyanide solution is acted on by magnesium with copious evolution of hydrogen and development of heat; and, if excess of magnesium is used, magnesium cyanide alone remains in solution; in this case the hydrogen can only result from the action of the metal on the water.

The black powder deposited on reducing solutions of gold or platinum chloride with magnesium is partially dissolved by dilute hydrochloric acid, yielding a solution containing the noble metal; in this case also, the first action consists in the formation of magnesium hydroxide, and the liberation of hydrogen which then more or less completely reduces the gold or platinum. On treating a cobalt, nickel, or ferric solution with magnesium, it is easy to see coloured flocks of the respective hydroxides floating in the liquid, and, as the action of the magnesium continues, these are gradually reduced to the metallic state. When magnesium acts on copper sulphate solution, a basic copper sulphate is first precipitated, and the magnesium becomes coated with a black powder; this, on treatment with dilute hydrochloric acid, turns red, and copper goes into solution. Magnesium acts slowly on potassium chloride solution, with formation of caustic potash and magnesium hydroxide; the alkaline liquid contains magnesium in solution. The first action in this case seems also to occur between the metal and the water.

It must, therefore, be concluded that with a few possible exceptions, such as those of lead, silver, and palladium, metallic magnesium does not immediately precipitate the metals from their solutions; the separation of the metals is due to the reduction of their hydroxides or basic salts by the hydrogen resulting from the decomposition of the water.

Potassium arsenite is reduced by magnesium with slow evolution of hydrogen containing hydrogen arsenide, arsenic being deposited. Potassium arsenate is also decomposed with evolution of hydrogen containing hydrogen arsenide, but a white deposit of insoluble magnesium arsenate is formed on the metal. The action of magnesium on arsenious and arsenic acids is very similar. The action of magnesium on the salts of the alkaloïds is quite in accordance with the conclusion stated above.

A slow evolution of hydrogen occurs on treating iodic acid solution with magnesium, and iodine is liberated, owing to reaction occurring between the iodic and hydriodic acids; the yellow colour due to the iodine disappears as the action continues, and the unstable magnesium hypoiodite is precipitated as a red-brown powder. The formation of the latter is due to reaction between magnesium hydroxide and iodine, as may be readily ascertained by direct experiment. Magnesium might well be used for the detection of iodic acid, just as hypoiodites can be used as reagents for magnesium salts.

Considerable quantities of magnesium dissolve in solutions of phenol and the dihydroxybenzenes, and the phenoxides and phenolates

of the heavy metals can be readily precipitated from the solutions by double decomposition.

W. J. P.

Structure and Constitution of Alloys of Copper and Zinc.

By GEORGES CHARPY (*Compt. rend.*, 1896, **122**, 670—672).—Alloys of copper and zinc, containing from 0 to 35 per cent. of the latter, all have the same micrographic characteristics, and the metal obtained by casting, consists of long, dendritic needles, the ramifications of which are often at right angles. If the metal is kept at a temperature somewhat below its melting point the crystals increase in size and distinctness, and take the form of macle octahedra, which are larger the higher the temperature at which the alloy has been heated.

When the proportion of zinc exceeds 34 per cent., the fused metal contains crystallites with rounded edges, but no dendrites, and the crystalline structure does not markedly develop on annealing. With a higher proportion of zinc, the crystallites tend to disappear, and with 45 per cent. the alloy consists of polygonal plates. With 67 per cent. of zinc, the alloy has a conchoidal fracture, and is practically homogeneous, although showing traces of imperfectly formed crystals.

In the alloys of a distinctly crystalline structure (0 to 34 per cent. of zinc), the impurities are localised between the crystals; they seem to consist of isomorphous mixtures of copper with the compound Cu_2Zn . The well-known fragility of brass that has been heated beyond 200° may be attributed to the development of the crystalline structure.

With the alloys containing 36 to 45 per cent. of zinc, this development of crystalline structure does not take place, and it is known that such alloys can be worked when hot; they are probably mixtures of the two compounds Cu_2Zn and CuZn_2 . Alloys containing more than 67.3 per cent. of zinc are probably mixtures of the compound CuZn_2 with zinc.

C. H. B.

Properties of Metals separated from their Amalgams.

By ANTOINE GUNTZ (*Compt. rend.*, 1896, **122**, 465—467).—Ramsay's experiments on the boiling point of mercury containing metals in solution show that at about 350° the molecular weight of the metals dissolved in the mercury coincide with their atomic weights (*Trans.*, 1889, 521), and Meyer's determinations of the E.M.F. of amalgams show that this is also the case at the ordinary temperature. It follows that if the mercury can be removed from the amalgams at a comparatively low temperature by distillation in a vacuum, the metals will be left more or less completely in an atomic condition. The author has previously shown (*Abstr.*, 1892, 582) that manganese extracted from its amalgam at a low temperature is more energetic than the metal in its ordinary form. Calorimetric determinations show that the heat of oxidation of this pyrophoric form is $+3.8$ Cals. greater than that of the ordinary metal. Ordinary metals are most probably highly polymerised, and hence show much lower chemical activity than when separated from their amalgams in an atomic, or at any rate in a less highly polymerised condition. Possibly a similar explanation holds good for the pyrophoric metals obtained by reduction.

C. H. B.

New and Abundant Source of the Rare Oxides of Thorium, Cerium, Yttrium, Lanthanum, Didymium, and Zirconium. By THOMAS L. PHIPSON (*Chem. News*, 1896, 145).—By heating finely pulverised Norwegian granite containing pink and white felspar and black mica with pure hydrochloric acid, diluting, nearly neutralising with ammonia, and adding excess of crystalline oxalic acid, which is dissolved by stirring, a precipitate is obtained containing cerium, zirconium or thorium, or both, and yttrium or lanthanum. The solution when quite neutralised with ammonia and treated with excess of oxalic acid, yields a further precipitate containing cerium, didymium, lanthanum, and yttrium. Nearly 2 per cent. of rare oxides and carbonates have been obtained in this way from the granite.

D. A. L.

Cerium Carbide. By HENRI MOISSAN (*Compt. rend.*, 1896, 122, 357—362).—Cerium carbide, C_2Ce ($Ce = 140$), is obtained as a reddish-yellow, crystalline, transparent substance of sp. gr. 5.23, by heating an intimate mixture of white cerium dioxide with one quarter of its weight of sugar carbon in the electric furnace until evolution of gas ceases and the product remains in quiet fusion. A current of 300 ampères and 60 volts will reduce 100 grams of the oxide in 8 or 10 minutes, whilst a current of 900 ampères and 50 volts will reduce 600 grams in three minutes. The carbide is not attacked by fluorine in the cold, but burns brightly in it on gently heating; it burns in chlorine at 220° , and in bromine and iodine vapours at somewhat higher temperatures, in oxygen and in sulphur vapour at a red heat, and in selenium vapour below dull redness. Phosphorus vapour or nitrogen has no action at the softening point of glass. Hydrogen chloride attacks the carbide at 650° , and hydrogen iodide at a higher temperature; hydrogen sulphide decomposes it at a red heat, but ammonia forms no nitride at 600° . Oxidising agents attack the carbide very readily, and fused alkali nitrates, chlorates, hydroxides, or carbonates decompose it with great energy. Concentrated sulphuric acid is reduced on heating, but concentrated nitric acid is without action.

Water decomposes the carbide with formation of cerium hydroxide and evolution of a gas which contains about 75 per cent. of acetylene, 4 per cent. of ethylene, and 21 per cent. of methane. Dilute acids behave similarly, and in all cases the proportion of acetylene varies with the conditions under which decomposition takes place.

C. H. B.

Carbides of Yttrium and Thorium. By HENRI MOISSAN and ÉTARD (*Compt. rend.*, 1896, 122, 573—580).—Yttria, which occurs together with the oxides of erbium, holmium, thulium, &c., in the minerals gadolinite, euxenite, and monazite, can be separated from them by treatment with sulphuric acid, and fractionally precipitating the dissolved metals as basic chromates, 10 fractions being taken; the last contains the yttrium; this is then converted into the oxalate, and finally into the oxide by ignition.

The yttria thus formed is powdered, mixed with sugar charcoal, and made into a paste with turpentine; it is then heated in the

electric furnace for five or six minutes, a current of 900 ampères and 50 volts being employed.

Yttrium carbide, YC_2 , forms fusible ingots showing a crystalline structure. Its density is 4.13 at 18° . Halogens act on it readily in the cold; it burns in oxygen and in the vapour of sulphur or of selenium, and is readily attacked by acids.

Water decomposes it with the production of a mixture of gases having the composition C_2H_2 , 71.7; CH_4 , 19.0; C_2H_4 , 4.8; H, 4.5; total, 100.0.

Thorium oxide occurs associated with iron and the metals of the cerium and yttrium groups in thorite and in orangite. The solution of the mixed oxides in hydrochloric acid is precipitated by means of oxalic acid, and the precipitate washed free from iron, &c. On treating the residual oxalates with a solution of ammonium oxalate, the thorium alone dissolves, and is separated by filtration.

Thorium carbide, ThC_2 , is produced in an analogous manner to the yttrium carbide, heating for four minutes, however, sufficing; it is a fusible, crystalline substance of sp. gr. = 8.96 at 18° , and closely resembles yttrium carbide in its properties; concentrated acids have, however, little action on it; in dilute acids it dissolves readily. Cold water decomposes it with the production of a mixture of gases having the composition

	C_2H_2 .	CH_4 .	C_2H_4 .	H.
I.	47.05	31.06	5.88	16.01
II.	48.44	27.69	5.64	18.23

J. F. T.

Deposition of Aluminium from Aqueous Solutions. By HENRY N. WARREN (*Chem. News*, 1896, **73**, 123).—Aluminium hydroxide is dissolved in hydrochloric acid, a large excess of tartaric acid is added, and then ammonia until a clear solution is obtained. Employing an aluminium or carbon positive electrode, a brass negative electrode, and a current of 9 ampères and 12 volts in this solution, the brass becomes plated with aluminium, and can be burnished, but when once the surface is covered, further deposition is considerably retarded.

D. A. L.

Alumina in Glass. By LÉON APPERT (*Compt. rend.*, 1896, **122**, 672—673).—The presence of alumina in glass prevents, or at any rate retards the devitrification which results from repeated heating. It also allows part of the potassium or sodium to be replaced by calcium with distinct advantages as regards solidity, resistance, and elasticity. Alumina can be substituted for silica to an extent not exceeding 7 or 8 per cent., and the glass becomes slightly more fusible, but its malleability is not appreciably affected. The only disadvantage arising from the introduction of the alumina is the increased colour due to its action on the ferric oxide. Pure clay or felspar is a convenient form in which to introduce the alumina.

C. H. B.

Manganese Carbide. By HENRI MOISSAN (*Compt. rend.*, 1896, **122**, 421—423).—The manganese carbide, Mn_3C , described by Troost and Hautefeuille, is obtained by heating a mixture of trimanganese tetroxide with one quarter of its weight of sugar carbon in a carbon

tube, closed at one end, in the electric furnace with a current of 350 ampères and 50 volts. The reaction is complete in a few minutes. The sp. gr. of the carbide is 6.89 at 17°. Fluorine attacks it in the cold, and chlorine on gently heating, hydrogen chloride below a red heat, and ammonia at a dull red heat, with production of a nitride. When gently heated, it burns in oxygen, nitrous oxide, or nitrogen peroxide. Dilute acids attack it readily with formation of liquid hydrocarbons, and water decomposes it with evolution of methane and hydrogen in practically equal volumes, neither liquid nor solid hydrocarbons being formed. C. H. B.

Nickel and Cobalt Borides. By HENRI MOISSAN (*Compt. rend.*, 1896, 122, 424—426).—Nickel boride, NiB, and cobalt boride, CoB, can be obtained by heating their constituents in crucibles, brasqued with boron, in an electric furnace with a current of 300 ampères and 50 volts, or in a reverberatory furnace fed with gas carbon. The product is treated with dilute nitric acid, and the borides are obtained in brilliant prisms which are often several mm. long, are magnetic, and about as hard as quartz. The sp. gr. of the nickel compound is 7.39 at 18°, and of the cobalt compound 7.25. They are attacked by chlorine at a dull red heat, by bromine at a higher temperature, and by iodine at the softening point of glass. They are not affected by dry air or oxygen, but alter rapidly in moist air, especially in presence of carbonic anhydride. Fused alkali chlorates, nitrates, hydroxides, or carbonates dissolve and decompose them; water vapour at a dull red heat converts them into oxides and boric acid, and acids, concentrated or dilute, attack them with varying degrees of readiness.

The nickel and cobalt borides are analogous to the iron borides previously described, and may likewise be used for introducing boron into a metal such as iron (compare Abstr., 1895, ii, 220 and 270).

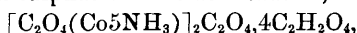
C. H. B.

Constitution of Cobalt, Chromium, and Rhodium Bases. VII. By SOFUS M. JØRGENSEN (*Zeit. anorg. Chem.*, 1896, 11, 416—453; see also Abstr., 1895, ii, 47).—The acid oxalo-sulphate of purpureo-cobalt described by Gibbs and Genth (*Smithson. Contrib.*, 1856, 32) is the sulphate of a series of oxalopurpureo-salts, which have the general formula $C_2O_4 \cdot \begin{matrix} NH_3 \\ Co \cdot [NH_3]_4 \cdot X \end{matrix}$.

The normal oxalo-sulphate of these authors has not the constitution assigned to it by them, but is a normal oxalopurpureosulphate; also the acid roseo-oxalate of Gibbs is an acid oxalopurpureo-oxalate, and yields an oxaloplatinochloride, which is not identical with roseo-cobalt-oxalate platinumochloride.

Pentamine-oxalopurpureocobalt salts are obtained by boiling the pentamine roseo-salts with a solution of oxalic acid; also by precipitating the solution obtained by boiling roseo-oxalates with oxalic acid, by the addition of various acids. They are especially prone to form acid salts, which are converted into the normal salts by the addition of ammonia. The acid sulphate, $C_2O_4 \cdot (Co_5NH_3) \cdot SO_4H, H_2O$, is obtained by dissolving equal weights of the roseosulphate and oxalic acid in warm

water and evaporating the solution to crystallisation on the water bath; also by adding dilute sulphuric acid to a solution of the acid oxalate and precipitating with 95 per cent. alcohol; also by heating a solution of the roseo-oxalate with oxalic acid on the water bath, adding dilute sulphuric acid to the cold mixture and then precipitating with alcohol. It crystallises in red leaflets, sometimes with $2\text{H}_2\text{O}$. It dissolves in dilute hydrochloric acid with a violet coloration, being completely converted into the chloropurpureochloride. It is not dissolved by cold concentrated ammonia; when boiled with dilute ammonia, it dissolves, but is not converted into the roseo-salt. With concentrated hydrobromic acid, a voluminous precipitate of the acid oxalopurpureobromide is obtained; it dissolves in 100 parts of cold water. The solution has an acid reaction, gives a voluminous precipitate with barium chloride and hydrochloric acid, but is not precipitated by calcium acetate. The *platinochloride* crystallises in reddish needles, the *aurochloride* in lustrous red, rhombic plates. The *normal sulphate*, $[\text{C}_2\text{O}_4(\text{Co}_5\text{NH}_3)]_2\text{SO}_4 \cdot 3\text{H}_2\text{O}$, crystallises in rose-red, microscopic needles, is sparingly soluble, has a neutral reaction, and gives the same compounds with sodium platinochloride and sodium aurochloride as the acid sulphate. The *acid oxalate*,



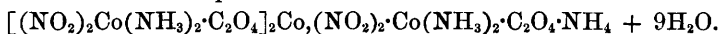
crystallises in red, six-sided tablets, the *normal oxalate* is a deep red precipitate consisting of very small octahedra, and is quite insoluble in cold water. The corresponding *iodides*, *chlorides*, *bromides*, and *nitrates* are also described.

Tetramine-oxalopurpureocobalt chloride, $\text{C}_2\text{O}_4 \cdot \text{Co}(\text{NH}_3)_4\text{Cl}$, is obtained by heating the aquotetramine chloride with oxalic acid and water on the water bath. The salt, which completely crystallises out on cooling, is washed with 50 per cent. and then with 95 per cent. alcohol. The crude aquotetramine chloride can be employed, since the praseochloride which is present is also converted into tetramine-oxalopurpureocobalt chloride, and a small quantity of pentamine purpureochloride is converted into acid *p*-oxalopurpureocobalt oxalate, which remains in the mother liquor. It crystallises in lustrous, carmine rhombic tablets, is not converted into roseo-salt when boiled with ammonia, dissolves in 140 parts of cold water with a carmine coloration and neutral reaction, and when shaken with freshly prepared silver oxide yields a strongly alkaline solution, containing tetramine-oxalopurpureocobalt hydroxide. This salt is identified as a tetramine oxalopurpureo-salt by the following reactions. The aqueous solution, when treated with silver nitrate, yields all its chlorine as silver chloride. It is not precipitated by calcium acetate and a small quantity of acetic acid. When dissolved in cold concentrated sulphuric acid and treated with concentrated hydrochloric acid it is converted into the praseochloride, which is reconverted into the original salt when heated with oxalic acid. The *platinochloride*, $[\text{C}_2\text{O}_4 \cdot \text{Co}(\text{NH}_3)_4]_2\text{PtCl}_6 + \text{H}_2\text{O}$, crystallises in scarlet quadratic tablets, and is insoluble in water and alcohol. The *platinosochloride*, $[\text{C}_2\text{O}_4 \cdot \text{Co}(\text{NH}_3)_4]_2\text{PtCl}_4 + 1\frac{1}{2}\text{H}_2\text{O}$, the *chloride*, *bromide*, *sulphate*, and *oxalate* are also described.

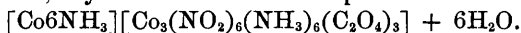
The salt, $\text{C}_2\text{O}_4 \cdot [\text{Co}(\text{NH}_3)_3] \cdot \text{Cl} + \frac{1}{2}\text{H}_2\text{O}$, is obtained by gently warming

the dichrochloride with a solution of oxalic acid, or by allowing the dichrochloride to remain in the cold with a concentrated solution of oxalic acid in water or dilute alcohol. It is an indigo-blue precipitate consisting of dichroitic rhombic tablets, and, when allowed to remain under water and exposed to light, dissolves sparingly with a red coloration.

When ammonium-diaminecobalt nitrite, dissolved in hot water, is heated with a saturated solution of oxalic acid for a few minutes on the water bath, nitrogen and oxides of nitrogen are evolved, and a brown crystalline precipitate is obtained which is most probably a *double salt* of the composition

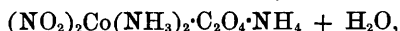


It crystallises in microscopic rhombic tablets, is soluble in 280 parts of cold water, and has a neutral reaction. When precipitated with a luteocobalt salt, it yields a salt of the composition



When treated with sodium hydroxide out of contact with the air, it yields a greenish-blue precipitate, which, on warming, is converted into red cobaltous hydroxide. The *silver salt*, with $9\text{H}_2\text{O}$, forms brown crystals similar to the ammonium salt, and contains 1Ag to 4Co . The *luteo-salt* is precipitated by adding various soluble luteo-cobalt salts to the cold saturated solution of the ammonium-cobalt salt. It crystallises with $6\text{H}_2\text{O}$, and when warmed with dilute nitric acid all the cobalt present as luteocobalt is precipitated as luteo-cobalt nitrate. The cobalt in the luteocobalt is to the cobalt in the complex salt as 1 : 3.

Ammonium-dinitrodiaminecobalt oxalate,



is obtained by mixing a solution of the ammonium-diamine nitrite with a solution of oxalic acid, both at 50° . Nitrogen and oxides of nitrogen are evolved, and the ammonium-cobalt salt is precipitated; after a time, more of the ammonium salt separates in larger crystals. The mixture is filtered, the ammonium salt washed out of the precipitate with cold water, and the solution mixed with the filtrate. The solution of the ammonium salt is then precipitated by the addition of ammonium chloride and washed with alcohol. It crystallises in rhombic prisms, dissolves with a beautiful brown coloration and neutral reaction in 30 parts of cold water, dissolves without change in dilute hydrochloric acid, and yields with solutions of metallic salts, brown crystalline precipitates. The *free acid* is obtained by treating the silver salt with hydrochloric acid. It reacts strongly acid, precipitates silver nitrate, and, when evaporated over sulphuric acid, is gradually decomposed with formation of the ammonium cobalt salt. The *sodium, silver, potassium, barium, ammonium-magnesium, ammonium cobalt, and luteocobalt salts* are described.

E. C. R.

Chromous Ammonium Carbonate. By GEORGES BAUGÉ (*Compt. rend.*, 1896, 122, 474—477).—Chromous ammonium carbonate,

$\text{CrCO}_3(\text{NH}_4)_2\text{CO}_3 + \text{H}_2\text{O}$, is obtained as a yellow, crystalline powder by passing carbonic anhydride into an ammoniacal solution of chromous acetate, or by boiling the solution with sodium carbonate. It is a powerful reducing agent, and alters rapidly in presence of air and moisture, although comparatively stable when carefully dried. Chlorine attacks the salt at a dull red heat, and hydrogen sulphide at a somewhat lower temperature converts it into black, crystalline chromium sesquisulphide. In absence of oxygen, dilute sulphuric and hydrochloric acids dissolve the carbonate, forming blue solutions.

C. H. B.

Preparation of Pure Molybdenum. By AD. VANDENBERGHE (*Zeit. anorg. Chem.*, 1896, **11**, 385—396).—An examination of the method for preparing pure molybdenum, described by Berzelius and Débray, which consists in reducing the pure trioxide in a current of hydrogen, shows that it is not without errors. When platinum vessels are employed, the molybdenum contains platinum and the vessels are contaminated with molybdenum; when porcelain is employed, the molybdenum contains distinct traces of molybdenum silicide. In order to remove these traces of silicon, the product must be washed with hydrofluoric acid, hydrochloric acid, and water, and dried in a vacuum. The product, which contains traces of the lower oxides of molybdenum, cannot be purified by heating in a current of dry hydrogen chloride; after heating the product at 200° in hydrogen chloride and then passing air through the apparatus until the evolved gas showed no traces of chlorine, the molybdenum was found to contain a distinct trace of chlorine. A sample of the molybdenum was then partially oxidised by heating in the air and treated with dry hydrogen chloride at 200° , when the result showed that only part of the lower oxides are removed by this method. When heated in dry hydrogen chloride at $500\text{--}600^\circ$, a reddish product is formed which is probably an oxychloride, and small quantities of hydrogen are evolved. Crystalline molybdenum dioxide, prepared by fusing a mixture of ammonium molybdate, molybdenum trioxide, borax, and potassium carbonate, is not altered even when heated very strongly in dry hydrogen chloride. The results show that by this method of purification only molybdic anhydride and oxides of the molybdenum molybdate type are eliminated.

The method described by von der Pfordten (*Abstr.*, 1884, 965), which consists in the reduction of molybdenum polysulphide in a current of hydrogen is only applicable when a few centigrams of the polysulphide are employed. Employing 15 grams of the dry polysulphide, the author finds that, after heating for 48 hours at a very high temperature, the product still contains traces of sulphur.

The reduction of calcium molybdate by heating it with carbon yields a product containing about 8 per cent. of carbon; Moissan's pure molybdenum, prepared by heating molybdenum oxide and carbon in the electric furnace, contains 0.08 to 0.28 per cent. of impurities.

The author reserves for future communication the description of a method for the preparation of chemically pure molybdenum.

E. C. R.

Action of Certain Gases on Heated Molybdenum. By AD. VANDENBERGHE (*Zeit. anorg. Chem.*, 1896, **11**, 397—403).—Pure dry hydrogen is without action on finely divided molybdenum. After heating a sample for two hours at the highest temperature of the furnace, no alteration in weight could be detected, and no formation of water was observed when the sample was further heated in a current of oxygen. Pure dry nitrogen is also without action on molybdenum. When molybdenum is heated at 200° in a current of pure dry carbonic anhydride, the latter is reduced to carbonic oxide and the molybdenum becomes covered with brown flakes. This is probably a reversible reaction as expressed in the equation $\text{MoO}_3 + \text{CO} \rightleftharpoons \text{CO}_2 + \text{Mo}$, for Muthmann (*Annalen*, **238**, 123) states that molybdic anhydride is reduced by carbonic acid not only to the lower oxides, but at higher temperatures to metallic molybdenum.

E. C. R.

Atomic Weight of Tungsten. By E. ROBERT SCHNEIDER (*J. pr. Chem.*, 1896, [2], **53**, 288—303).—The author's determinations of the atomic weight of tungsten (*J. pr. Chem.*, 1850, **50**, 152) by the reduction of tungstic acid in hydrogen and by the oxidation of tungsten in the air, lead to a mean value of 184.12. Later, Marchand found 184.1, and this was confirmed by Dumas. Recently Pennington and Smith and Smith and Desi (*Abstr.*, 1895, ii, 230) have given the values 184.92 and 184.70 by the oxidation method and the reduction method respectively. They account for the fact that their numbers are higher than that formerly accepted by supposing that the tungstic acid previously used contained molybdic acid. The author points out that this is extremely improbable; for if it were the cause of difference there would have had to be 1 per cent. of molybdic acid present, an amount which he could not have overlooked. To assure himself of the accuracy of his former work, he has repeated the experiments, and as a mean of three oxidations and three reductions, has obtained the value 184.01, and has satisfied himself as to the absence of molybdic acid. In criticising the work of Pennington and Smith, the author points out that they have neglected the sole means available for the detection of constant errors, namely, the use of widely differing weights of the material experimented with. Furthermore, they ignited their tungsten to oxide in an open crucible for 10 hours, and they neglected to use a surface counterpoise while weighing. Analogous errors underlie the work of Smith and Desi.

A. G. B.

A New Zirconium Carbide. By HENRI MOISSAN and LENGFIELD (*Compt. rend.*, 1896, **122**, 651—654).—In order to obtain zirconium oxide, powdered zircon is mixed with sugar-carbon, and heated in a carbon crucible in the electric furnace for 10 minutes with the arc from a current of 1000 ampères and 40 volts. The greater part of the silica volatilises and impure zirconium carbide is left. This is heated in chlorine, and the mixture of zirconium chloride with iron and silicon chlorides is boiled with concentrated hydrochloric acid, and almost pure zirconium chloride separates. After further purification, it is converted into oxide by precipitation.

Zirconium carbide, ZrC , is obtained by placing a mixture of the oxide with sugar-carbon in a carbon tube closed at one end and heating it in the electric furnace with an arc from a current of 1000 ampères and 50 volts. It has a grey colour and a metallic lustre, scratches quartz but not rubies, and is not attacked by dry or moist air even at 100° . It burns in fluorine in the cold, chlorine at 250° , bromine at 300° , and iodine at about 400° , and it is readily attacked by halogen hydracids. At a dull red heat, it burns brilliantly in oxygen, and is slightly attacked by sulphur vapour at the same temperature. Water, ammonia, and hydrochloric acid do not attack the carbide even when strongly heated. Nitric and sulphuric acids attack it, and oxidising agents such as potassium chlorate, nitrate, or permanganate, as well as the hydroxide, decompose it readily, but fused potassium cyanide is without action. C. H. B.

Action of Nitric Peroxide and Air on Bismuth Chloride. By V. THOMAS (*Compt. rend.*, 1896, **122**, 611—613).—On passing dry nitric peroxide over bismuth chloride, also carefully dried, contained in a weighed flask, it is readily absorbed, the chloride becoming yellow. The compound, BiCl_3NO_2 , is yellow, and is readily decomposed by water and moist air.

The action of this gas at higher temperatures is, however, quite different, the chloride being then oxidised to the oxychloride. To this oxychloride the author attributes the formula BiOCl , and not $\text{Bi}_3\text{Cl}_3\text{O}_2$. J. F. T.

Fusibility of Platinum in a Wind Furnace fed with Carbon. By VICTOR MEYER (*Ber.*, 1896, **29**, 850—852).—It has never previously been proved that platinum can be fused by the heat of a wind furnace fed with carbon, when it is so situated as to be protected from the gases produced by the combustion, and from particles of carbon (*Hecht, Chem. Zeit.*, 1896, 85). This was, however, accomplished by the author, who enclosed the platinum in a cavity in a piece of fire-resisting clay, and exposed the whole to the heat of a wind furnace fed with retort graphite. On breaking open the mass after the experiment, the platinum was found in the form of a sphere, whilst a piece of platinum-iridium alloy, containing 25 per cent. of iridium, which had been placed in an adjoining cavity in the block, was quite unaltered in shape and lustre. A. H.

Mineralogical Chemistry.

Native Gold from Eule, Bohemia. By FRANZ ŠTOLBA (*Verh. k. k. geol. Reichsanst.*, 1893, 64; from *Böhm. Zeits. chem. Indust.*, 1893, 3, 1).—The native gold which occurs as threads, grains, and scales, together with pyrites, mispickel and stibnite, in quartz and calcite veins in the Archæan rocks at Eule, Bohemia, gave the following results on analysis.

Au.	Ag.	Fe.	Cu.
91.34	8.42	0.16	0.02

The purest gold from this locality contains 95.8 per cent. Au.

L. J. S.

Microchemical Reactions of Minerals of the Lamprite Group. By JOHANN LEMBERG (*Zeits. deutsch. geol. Ges.*, 1894, **46**, 788—799).—This group includes opaque, lustrous minerals; those treated of being mostly sulphides, but also arsenic, arsenolite, tetrahedrite, and pharmacolite. The action of an alkaline bromine solution and of a silver sulphate and sulphuric acid solution on each of these minerals, when in polished sections, is described in detail; the variations in the reactions being sufficient to be used for purposes of discrimination. With the bromine solution, some minerals are dissolved, others are very slowly attacked, whilst others are oxidised. With the silver solution, metallic silver or silver sulphide, or both, are deposited on the minerals.

L. J. S.

Quiroguite. By (L.) FERNÁNDEZ NAVARRO (*Anales Soc. Española Hist. Nat.*, 1895, **24**, Actas 96—100).—This mineral, named after F. Quiroga, occurs with anglesite, siderite, and pyrites, at the mines San Andrés, Georgiana, Paraíso, &c., in the Sierra Almagrera, Spain. From the habit of the pyramidal crystals the system is given as tetragonal, but some of the measured angles agree closely with those required for cubic symmetry; and Schrauf suggests that the crystals are probably only galena, in which eight of the faces of a triakis-octahedron are developed to the exclusion of the remainder, thus forming an acute square pyramid. The basal cleavage is, however, stated to be more perfect than the two which are perpendicular to it; and thermal conductivity experiments are said to support the view that the mineral is tetragonal. Colour, lead-grey; sp. gr. 7.22; H = 3. Analysis by F. Soria gave

Pb.	Sb.	Fe.	S.	Ag.	Total.
63.89	9.69	6.30	17.51	trace	97.39

From this is deduced $(\text{PbS})_{30}(\text{Sb}_2\text{S}_3)_4(\text{FeS})_{11}$, or, as pyrites was seen enclosed in the crystals, $(\text{PbS})_{23}(\text{Sb}_2\text{S}_3)_3$.

L. J. S.

Composition of Bauxites. By FRANCIS LAUR (*Trans. Amer. Inst. Min. Eng.*, 1895, **24**, 234—242).—Although the commercial bauxites vary considerably in composition and physical characters, it is pointed out that the alumina is fairly constant (66—69 per cent.) and that the sum of the variable constituents, water, silica, and ferric oxide, is also constant (27 per cent.); the various accessory constituents (titanium, vanadium, &c.) also showing a constant total of 3 or 4 per cent. According as the amount of the variable constituents vary, the following types are distinguished.

Pure or hyaline bauxite.....	$\text{Al}_2\text{O}_3 + 2\text{H}_2\text{O} +$	accessories.
Pale bauxite of Villeveyrac ..	$\text{Al}_2\text{O}_3 + (\frac{1}{2}\text{H}_2\text{O}, \frac{1}{2}\text{SiO}_2) +$	„
Maximal siliceous bauxite....	$\text{Al}_2\text{O}_3 + \text{SiO}_2 +$	„
Red bauxite of Var	$\text{Al}_2\text{O}_3 + (\frac{1}{2}\text{H}_2\text{O}, \frac{1}{2}\text{Fe}_2\text{O}_3) +$	„
Maximal ferruginous bauxite.	$\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3 +$	„
Mixed bauxite of Baux	$\text{Al}_2\text{O}_3 + (\frac{1}{3}\text{H}_2\text{O}, \frac{1}{3}\text{SiO}_2, \frac{1}{3}\text{Fe}_2\text{O}_3) +$	accessories.

The hydrate thus passing hypothetically into silicate and aluminate.

L. J. S.

Hæmatite from Elba. By R. ROHRER (*Tsch. Min. Mitth.*, 1895, 15, 184—187).—In the following analyses, the mineral was reduced by hydrogen.

	Fe_2O_3 .	SiO_2 .	CaO .	MgO .	Total.
I.	98·58	0·51	0·38	0·73	100·20
II.	98·63	0·47	0·45	0·74	100·29

Manganese and ferrous iron are absent, and there is no loss on ignition. In the same volume (p. 68), E. A. WÜLFING gives the refractive indices and the sp. gr. (5·285) for the same material.

L. J. S.

Magnetic Iron Hydroxide. By H. BERNHARD KOSMANN (*Zeits. deutsch. geol. Ges.*, 1893, 45, 508—509).—Brown iron ore, occurring with chrome iron ore at Harteberg, near Grochau, in Silesia, gave, on analysis,

Fe_2O_3 .	Al_2O_3 .	MnO_2 .	$(\text{Co}, \text{Ni})\text{O}$.	Cr_2O_3 .	CaO .	MgO .
32·20	17·10	2·00	0·04	0·41	0·03	0·02
	SiO_2 .	H_2O (at 150°).	H_2O (on ignition).		Total.	
	36·94	8·01	2·40		99·16	

The mineral is strongly magnetic, this property being ascribed to a “peculiar molecular grouping,” as ferrous oxide is absent.

L. J. S.

Analyses of Bavarian Minerals, &c. By ADOLPH SCHWAGER and C. WILHELM VON GÜMBEL (*Geognost. Jahresh., München*, 1895, 7, 57—94).—Numerous analyses are given of ores, impure minerals, rocks, coals, waters, lake muds, laterite, loess, &c., mostly from Bavarian localities. The following are of interest.

Ilmenite.—Large tables, surrounded by white leucoxene, in a light-coloured diabase-like rock (leucophyre) from Köditz, in the Fichtelgebirge.

TiO_2 .	$\text{FeO}(\text{Fe}_2\text{O}_3)$.	MnO .	MgO .	Total.
46·33	48·85	1·27	1·84	98·29

Fahlore (Tennantite).—Light-coloured, from Hütttau, Salzburg.

Cu.	Fe.	Zn.	Ni, Co.	S.	As.	Sb.	Total.
46·65	6·56	0·71	0·11	28·21	13·94	4·65	100·83

Orthoclase.—I, porphyritic, twinned crystals, in granite, from Ochsenkopf; II, as lenticular aggregations with quartz and chlorite

in phyllite, from Rehau; III, whitish, and IV, reddish, in pegmatite, from Wellerthal; all in the Fichtelgebirge.

Labradorite.—V, in a gabbro-like rock, from Eschelkamm, Oberpfalz.

Diallage.—VI, blackish-brown, with numerous dark lamellate enclosures; from the same rock as V.

Muscovite.—VII, large plates from the pegmatite of Wellerthal (Nos. III and IV).

Hygrophilite.—VIII, white nodules in a red clay slate, from Reuschbach, Rhenish Bavaria; in water it falls to very fine scales; incompletely dissolved by caustic potash, probably owing to the presence of impurities.

	I.	II.	III.	IV.	V.	VI.	VII.	VIII.
SiO ₂	65.50	64.50	65.12	65.04	53.41	51.14	45.28	56.64
TiO ₂	—	—	—	—	—	4.01	—	—
Al ₂ O ₃ ..	19.82	19.41	19.56	19.23	29.22	4.06	37.59	26.68
Fe ₂ O ₃ ...	0.12	1.49	0.16	0.16	1.27	7.69	1.18	1.68
FeO.....	—	—	—	—	—	4.01	—	—
MnO....	—	—	—	—	—	1.12	—	0.12
CaO....	0.11	0.88	0.26	0.22	12.11	20.44	0.09	0.22
BaO....	0.31	—	—	—	—	—	—	—
MgO ...	0.07	0.02	0.09	0.09	0.44	8.16	0.17	0.29
K ₂ O ...	12.64	13.97	12.96	13.25	0.49	—	10.32	5.33
Na ₂ O ...	1.77	0.69	2.16	1.74	3.17	—	1.20	0.64
Loss on ignition }	0.32	0.30	0.32	0.36	0.33	0.35	4.12	7.13
Cl.....	0.01	—	—	—	—	—	—	—
Total..	100.67	101.26	100.63	100.09	100.44	100.98	99.95	98.73
Sp. gr...	2.580	—	2.572	to 2.580	2.702	3.251	2.930	2.415 2.554

Analyses are also given of sericite, chlorites, analcite, dopplerite, &c.
L. J. S.

Pyroxene from Renfrew. By ERNST A. WÜLFING (*Tsch. Min. Mitth.*, 1895, 15, 29—48).—A specimen labelled "hedenbergite, Renfrew, New Jersey," is shown to differ in its optical characters from the diopside-hedenbergite series. There is a strong dispersion of the acute bisectrix, which it is suggested may be connected with the presence of sesquioxide bases. After separating the numerous brown inclosures, the mean of two analyses gave

SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	FeO.	MnO.	CaO.	MgO.	Total.	Sp. gr.
49.94	4.25	4.76	5.15	0.50	23.29	12.54	100.43	3.38

The small amount of sodium and combined water present may occur in an acmite molecule, which will account for the 1.44 per cent. of SiO₂ in excess of that required by the formulæ RO₂SiO₂, and RO₂R₂O₃SiO₂. The optical constants for light of various wavelengths are determined; the extremes are

Light.	Extinction angle ($\epsilon : a$).	2V.	α .	β .	γ .
B.....	60° 58'	61° 34'	1·6928	1·6990	1·7169
G.....	59 51	59 12	1·7218	1·7278	1·7467

L. J. S.

Albite from Crete. By C. VIOLA (*Tsch. Min. Mitth.*, 1895, **15**, 135—158).—The colourless, transparent crystals of albite from Lakous, Island of Crete, are of interest as being almost pure $\text{NaAlSi}_3\text{O}_8$. The crystallographic constants are given as $a:b:c = 0.635:1:0.557$; $\alpha = 94^\circ 14' 30''$, $\beta = 116^\circ 31' 45''$, $\gamma = 88^\circ 5' 1''$ the optical constants as, extinction on b , $21\frac{1}{2}^\circ$; on c , $3\frac{1}{2}^\circ$; $2F = 123^\circ 2'$.

The analysis by E. Mattiolo gave

SiO_2 .	Al_2O_3 .	Na_2O .	K_2O .	Loss on ignition.	Total.	Sp. gr.
68·51	19·83	11·74	0·16	0·15	100·39	2·621

Traces of magnesia, iron, and manganese are due to microscopic enclosures of chlorite, which also, together with commencing decomposition in places, accounts for the loss on ignition. L. J. S.

Zoisite from Styria. By ST. LOVREKOVIĆ (*Mitth. Ver. Steiermark*, 1893, **29**, 296—306).—In the zoisite-amphibolite and the zoisite-garnet-amphibolite of Deutsch-Landsberg are veins of zoisite containing also quartz, hornblende, and here and there mica and epidote. The needles of zoisite from these veins gave, on analysis,

SiO_2 .	CaO .	FeO .	Al_2O_3 .	Loss on ignition.	Total.
42·05	18·92	6·49	29·97	2·53	99·96

L. J. S.

Wernerite (Dipyre) from Breno, Lombardy. By WILHELM SALOMON (*Tsch. Min. Mitth.*, 1895, **15**, 159—183).—In the Trias limestones around the mass of igneous rock (tonalite) of the Adamello Mountains, are found two varieties of scapolite; one occurs as black, or dark-green, regular prisms, without end-faces, in more or less aluminous limestones, sp. gr. 2·668; the other as colourless, irregular prisms, resembling tremolite, in a granular marble; sp. gr. 2·68. Analysis of the former, on material separated by means of hydrochloric acid and heavy solutions, gave

SiO_2 .	Al_2O_3 .	Fe_2O_3 .	CaO .	MgO .	K_2O .	Na_2O .	Loss on ignition.	Total.
52·74	23·98	0·40	7·43	2·77	1·86	9·00	1·18	99·36

Cl, SO_4 , and CO_2 were not determined. This gives the formula $3(\text{Ca}, \text{Mg}, \text{Na}_2, \text{K}_2)\text{O}, 2\text{Al}_2\text{O}_3, 8\text{SiO}_2$, or Me_3Ma_7 , that is, the meionite and marialite molecules in the proportion 5:7). The calcite enclosures are often as elongated rods parallel to the vertical axis of the crystal, and are mostly collected in the centre or in zones. The mineral, which is associated with magnetite, pyrites, pyrrhotite, muscovite (?), tremolite, and wollastonite, is confined to the outer zone of metamorphism, 700—1500 metres from the igneous mass; the inner zone containing garnet, idocrase, &c., but no dipyre.

A summary is given of the literature of "dipyre," and from the various analyses the formulæ MeMa_3 , MeMa_2 , MeMa , and Me_3Ma_7 are derived, thus showing that scapolite minerals described under this name belong partly to wernerite (of Dana), and partly to mizzonite, and that the name "dipyre" can only be applied to crystals of a certain habit, namely, thin prisms which are seldom terminated and are generally opaque.

L. J. S.

Moldavite from Bohemia. By JOSEPH HANAMANN (*Verh. k.k. geol. Reichsanst.*, 1894, 194; from *Böhm. Zeits. chem. Indust.*, 1893, 3, 365).—Moldavite from Wittingau gave, on analysis,

SiO_2 .	Al_2O_3 .	FeO .	MnO .	CaO .	MgO .	K_2O .
81.20	9.65	2.25	0.11	2.65	1.80	2.34

The glassy, transparent masses are of a dark olive green, and contain numerous gas-pores; sp. gr. 2.355, $H = 7$. It is regarded as an obsidian (pseudochrysolite) derived by the metamorphism of glassy felspar rich in silica. The peculiar puckered surface is taken to show that the masses are not water-worn pebbles. (Compare Abstr., 1894, ii, 241.)

L. J. S.

Glauconite from Co. Antrim. By A. PERCY HOSKINS (*Geol. Mag.*, 1895, [4], 2, 317—321).—Dark green grains (rather less than 1 mm. diameter) of glauconite separated from a calcareous sandstone in the Upper Greensand at Woodburn, Carrickfergus, Co. Antrim, gave, on analysis,

SiO_2 .	Al_2O_3 .	Fe_2O_3 .	FeO .	CaO .	MgO .	K_2O .	Na_2O .	H_2O .	Total.
40.00	13.00	16.81	10.17	1.97	1.97	8.21	2.16	6.19	100.48

Here the percentage of silica is lower than usual. The variations in composition of glauconite are discussed.

L. J. S.

Cobalt in the Sands of Woluwe-Saint-Lambert. By J. CROCC (*Bull. Acad. Belg.*, 1894, [3], 28, 485—498).—In the tertiary sands of the parish of Woluwe-Saint-Lambert, near Brussels, is a blackish or brownish substance coating the grains of sand; the sand thus blackened (with about 1—7 per cent. of the black substance) occurs as spots, beds, or more often in stem-like forms, evidently due to the infiltration of water from which the black substance was deposited. Analysis I is of the dark green hydrochloric acid solution of one sample; when this material is boiled with sulphuric acid, a purple coloured solution is obtained, showing the presence of Mn_3O_4 ; formula, $\text{Fe}_2\text{O}_3 + 2(\text{Mn}_3\text{O}_4, \text{CoO}) + 4\text{H}_2\text{O}$, or considering the iron to be present as admixed limonite, $(\text{MnO}, \text{CoO}) + \text{Mn}_2\text{O}_3 + 4\text{H}_2\text{O}$.

	Fe_2O_3 .	Mn_3O_4 .	CoO .	H_2O .	Total.
I.	20.952	41.873	4.761	32.379	99.964
II.	33.28	24.63	2.05	40.02	99.98

Analysis II is of the pulverulent substance from another point in the district; with this material no purple coloration was obtained with sulphuric acid; formula, $\text{Fe}_2\text{O}_3 + (\text{Mn}_2\text{O}_3, \text{CoO}) + 4\text{H}_2\text{O}$, or, elimi-

nating limonite, $(\text{MnO}, \text{CoO}) + \text{MnO}_2 + 4\text{H}_2\text{O}$. Copper, which was found by Rammelsberg in asbolite from Kamsdorf, Thuringia, is here absent.

L. J. S.

Limestones of Sussex Co., New Jersey. By FRANK L. NASON (*Amer. Geol.*, 1894, **13**, 154—164).—Several analyses are given of the white crystalline limestones in which occur the franklinite deposits of Sussex Co., N.J. They usually contain about 40 per cent. of magnesium carbonate, and thus approach true dolomites; when, however, they are in contact with the granite dykes there is only a little magnesium carbonate, but they here contain chondrodite, phlogopite, tremolite, and tourmaline. Farther from the granite, these white crystalline limestones pass into grey dolomitic limestones.

L. J. S.

Limestone from Koněprus, Bohemia. By FRANZ ŠTOLBA (*Verh. k.k. geol. Reichsanst.*, 1894, 195; from *Böhm. Zeits. chem. Indust.*, 1893, **3**, 336).—Analyses of this Devonian (f_2) limestone show over 99 per cent. CaCO_3 ; it occurs in large masses of uniform quality, and is the purest of Bohemian limestones.

L. J. S.

Mineral Waters from Styria. By ANTON FRITZ REIBENSCHUH (*Mitth. Ver. Steiermark*, 1893, **29**, 262—274).—Water from the Semlitsch Spring at Radein gave in 10,000 parts: K_2SO_4 , 0.12248; KCl , 0.02516; NaCl , 0.03537; NaHCO_3 , 0.51914; $\text{CaH}_2(\text{CO}_3)_2$, 3.42971; $\text{MgH}_2(\text{CO}_3)_2$, 1.31306; $\text{FeH}_2(\text{CO}_3)_2$, 0.37031; Al_2O_3 , 0.05371; SiO_2 , 0.59744; CO_2 , 20.65818 = 27.12456, also traces of strontium and lithium; sp. gr. 1.0006 at 14° . Other waters from the same region in S.E. Styria are mentioned.

L. J. S.

Water from the Klebelsberg Spring, Ischl. By H. DIETRICH (*Jahrb. k.k. geol. Reichsanst.*, 1893, **43**, 275—280).—This spring was met in the workings of the salt and anhydrite deposits at Ischl in Upper Austria. Analysis gave in 1,000 parts: K_2SO_4 , 0.04542; Na_2SO_4 , 0.37191; CaSO_4 , 0.21089; SrSO_4 , 0.00130; BaSO_4 , 0.00059; CaCO_3 , 0.01800; MgCO_3 , 0.02980; FeCO_3 , 0.00391; MgCl_2 , 0.32526; NaCl , 4.53387; LiCl , 0.00694; $\text{Ca}_3(\text{PO}_4)_2$, 0.00184; Al_2O_3 , 0.00335; SiO_2 , 0.01250; CO_2 (in bicarbonates) 0.02500; CO_2 (free), 0.04200 = 5.63258. Sp. gr. 1.00526 at 15° .

L. J. S.

Mineral Water from Radein, Styria. By ANTON FRITZ REIBENSCHUH (*Mitth. Ver. Steiermark*, 1894, **30**, 358—369).—Water from the Radein "Sauerbrunnen" gave in 10,000 parts:— K_2SO_4 , 3.1124; Na_2SO_4 , 0.5385; NaCl , 6.2939; NaHCO_3 , 43.1778; LiHCO_3 , 0.4973; $\text{CaH}_2(\text{CO}_3)_2$, 5.7473; $\text{MgH}_2(\text{CO}_3)_2$, 3.4991; $\text{FeH}_2(\text{CO}_3)_2$, 0.2386; Al_2O_3 , 0.0092; SiO_2 , 0.2004; CO_2 , 30.6210 = 93.9355; also traces of phosphoric acid and strontium; sp. gr. 1.00564 at 15° .

L. J. S.

Variation in Composition of Mineral Waters at Different Periods. By C. REMIGIUS FRESENIUS (*Jahrb. Nassau. Ver. Naturk.*, 1894, **47**, 13—23).—Analyses of various mineral waters of Nassau made at different periods are compared. Several analyses are quoted

of the water of the Niederselters Spring, the earliest being that of Westrumb (1794), and Fresenius' own dating from 1845 to 1863; the maximum and minimum amounts of the constituents per 1,000 parts of water are

	NaCl.	Na ₂ CO ₃ .	CaCO ₃ , SiO ₂ , &c.	Total solids.
Maximum ..	2.3542	0.8739	0.6719	3.8407
Minimum ...	2.0159	0.7903	0.5481	3.3543

The minima all occur in Fresenius' analysis of 1859, and the maxima (except of the Na₂CO₃) in his analysis of 1861. Although there have been slight variations in the concentration and relative amounts of the constituents, the character of the water has remained unchanged for a long period. It is pointed out that after wet seasons the concentration has been greater. In other waters there has been less variation the higher the temperature, this being due to the water being of deep-seated origin, and thus less liable to be affected by surface agencies. Below is given the ratio of the maximum (= 100) and minimum amounts of the total solids in the analyses compared.

	Temperature.	
Niederselters	15.5°	100 : 87.3
Kränchen, Ems.	36.0	100 : 95.9
Kesselbrunnen, Ems. ...	47.0	100 : 98.9
Kochbrunnen, Wiesbaden	68.5	100 : 99.7

L. J. S.

A Salt Lake in the Transvaal. By EMIL COHEN (*Tsch. Min. Mitth.*, 1895, 15, 1—8, and 194—195).—This small salt lake or pan, situated to the north of Pretoria, lies in a deep funnel-shaped depression in granite; besides rock salt, trona and some calcite occur, but no gypsum, although the latter is abundant in the ordinary salt pans of South Africa, these occurring in shallow depressions in sedimentary rocks. A sample of the water of sp. gr. 1.179, analysed by H. Hopmann, contained 21.14 per cent. of solids, consisting of Na₂CO₃, 27.25; NaCl, 72.70; Na₂SO₄, 0.05 per cent.; also traces of B₂O₃. Various suggestions are made to account for the origin of this pan.

L. J. S.

Physiological Chemistry.

Detection of Argon in the Air Bladder of Fishes and Physalidæ. By TH. SCHLOESING, jun., and JULES RICHARD (*Compt. rend.*, 1896, **122**, 615—617).—An analysis of gas contained in the air bladder of different varieties of fish taken from various depths is given in the following table.

	Polyprion. Cernium V.	Physalia.	Muraena helena L.	Synaphobranchus pinnatus Gr.		
Depth ..	Surface.	Surface.	88 m.	900 m.	1385 m.	
CO ₂ ...	2.2	0.0	6.4	3.1	0.0	3.6
O	18.8	12.2	73.1	75.1	78.4	84.6
N	79.0	87.8	20.5	21.8	21.6	11.8

Absorbing the carbonic anhydride and oxygen, and finally the nitrogen, by sparking over potash, the amount of the residual argon was found to be as follows.

	Physalia.	Muræna.	Synaphobranchus.
Argon	1·18 p. c.	1·85 p. c.	1·94 p. c.
			J. F. T.

Nutrition of Frog's Heart. By ARTHUR H. WHITE (*J. Physiol.*, 1896, 19, 344—355).—Serum albumin is regarded as the only proper nutrient for the frog's heart. If the heart is removed from the body and fed by the usual perfusion apparatus, with a saline solution, a stage is at last reached when all the blood is washed out from its interstices; and then no stimulus, or no amount of feeding, will cause it to contract, that is to say, it cannot contract at the expense of its own substance. It is only when it is in this condition that the test can be applied as to what is really a nutrient fluid. The true nutrients, that is, those capable of restoring the heart, are those which, like blood, serum, and lymph, contain both the serum proteids and salts.

W. D. H.

A New Hæmoglobinometer. By GEORGE OLIVER (*Proc. physiol. Soc.*, 1896, 15—16).—The blood is suitably diluted and placed in a shallow blood cell, where it rests on a white background made of precipitated calcium sulphate.

It is then compared with standard gradations arranged as a number of circular discs on a slab. The colours of these have been in all cases matched by Lovibond's colour-standard glasses. A separate set of standards is required for candlelight.

Observations of the blood cell and the standards are made through a camera.

W. D. H.

Estimation of the Number of Blood Corpuscles. By GEORGE OLIVER (*Proc. physiol. Soc.*, 1896, 16).—When the long diameter of a flattened tube filled with water is directed towards a candle flame, a transverse line of light is seen, made up of closely packed, minute images of the flame produced by the longitudinal fibrillation of the glass. When a measure of blood (10 cubic mm.) is washed into such a tube by Hayem's or other fixing fluid, the illuminated line is shut out of view, until, at a certain degree of dilution, it can just be detected as a faint streak. The amount of dilution is a delicate indicator of the percentage of corpuscles, and the tube can be graduated by comparison with an apparatus for counting the corpuscles.

W. D. H.

Coagulation of Blood. By R. M. HORNE (*J. Physiol.*, 1896, 19, 356—371).—The soluble salts of calcium, strontium, and barium retard or prevent the coagulation of the blood when present in the proportion of 0·5 per cent. and upwards. Barium salts are the most powerful in this direction (0·25 per cent. of barium chloride is sufficient), calcium the least.

Calcium hydroxide in saturated aqueous solution does not retard, strontium only slightly retards, whilst barium hydroxide is highly effective in retarding blood coagulation. This influence is overcome

in all cases by dilution with distilled water, or by the addition of a suitable amount of potassium oxalate. Coagulation delayed in the way described is accelerated by a temperature of 30—40°.

The chlorides of sodium and potassium, added to the extent of 0·07 per cent. and upwards, still further retard the coagulation of such mixtures.

W. D. H.

Absorption of Fluids from Connective Tissue Spaces. By ERNEST H. STARLING (*J. Physiol.*, 1896, 19, 312—326).—Salt solutions isotonic with the blood plasma can be, and are, absorbed directly from the blood vessels. This statement probably holds good for dropsical fluids containing small percentages of proteid. A backward filtration into the vessels is mechanically impossible in the connective tissue of the limbs, of the muscles, and of glands (similar in structure to the submaxillary).

The proteids of serum have an osmotic pressure equal to 30—40 mm. of mercury. Absorption of isotonic salt solutions by the blood vessels is determined by this osmotic pressure of the serum proteids. The same factor is probably responsible for the absorption from the tissues which ensues on any general lowering of capillary pressures, such as artificial anæmia. The proteids of the tissue fluids, when not used up in the tissues themselves, are probably absorbed mainly, if not exclusively, by the lymphatic system.

If the term “molecular imbibition” of Hamburger is replaced by osmotic pressure of the proteids of the tissues and the blood, the explanation of absorption given above is practically identical with that proposed by this observer.

W. D. H.

Extirpation of Salivary Glands. By EDWARD A. SCHÄFER and B. MOORE (*Proc. physiol. Soc.*, 1896, 13—14).—From the result of an experiment on a dog, the conclusion is drawn that the salivary glands do not exert any great metabolic influence apart from their external secretion, as does the pancreas.

W. D. H.

Iron in the Liver and Spleen. By RALPH STOCKMAN (*Brit. Med. J.*, 1896, i, 1077—1079).—The liver contains a store of iron, combined with nucleo-proteid in various degrees of intimacy. This is a reserve store which is called on after hæmorrhage, or when the dietary is poor in iron. An average dietary contains 6 to 11 milligrams of iron, which just about balances the daily loss. The normal liver contains in the mean 0·08 gram of iron per 100 grams of the dried organ, this number being derived from analyses detailed in the present research, together with those made by other observers. In general terms, the same is true for the spleen, only as it is impossible to obtain this organ free from blood, it is difficult to estimate the amount of iron in the blood-free organ; it is, however, less than in the liver.

A number of analyses are given of livers and spleens from cases of disease associated with different forms of anæmia; in most, the amount of iron is considerably diminished, although the organs are

never entirely free from the element. The most striking exception to this is seen in cases of pernicious anæmia where the iron is in excess.

It is held that pernicious anæmia is not a disease *sui generis*, but a manifestation seen in many fatal conditions associated with intense anæmia. These conditions are, moreover, associated with the occurrence of capillary hæmorrhages in many organs; and it is to these, and not to a special form of blood destruction, that the excess of iron in the organs is due.

W. D. H.

Chemistry of Vegetable Physiology and Agriculture.

Behaviour of the Leguminous Nodule Bacteria towards Caustic Lime. By BRUNO TACKE, and others (*Mitt. Ver. Förd. Moorkultur*, 1895, **13**, 389—399).—In consequence of the failure of soil inoculation on land to which lime had been applied, as compared with the results obtained with marl (Salfeld, this vol., ii, 332), it was decided to investigate the action of lime on nodule bacteria by means of pot experiments. Two soils were selected, (1) a sandy soil, and (2) a peaty soil, of the following composition (per cent. in dry matter).

	Loss on ignition.	Nitrogen.	Ash.	K ₂ O.	CaO.	MgO.	Fe ₂ O ₃ . Al ₂ O ₃ .	P ₂ O ₅ .	SO ₃ .
1.	4.43	0.16	95.57	0.05	0.03	0.02	0.82	0.07	0.04
2.	89.73	1.42	10.27	0.07	0.23	0.20	0.97	0.13	0.31

The soils received mineral manures, with lime, 15 or 20 grams, corresponding with about 24 or 32 cwt. per acre, and with marl respectively; and suitable soil was added for inoculating for peas, which were the plants to be grown. Some pots were left without inoculation. The results were as follows: sandy soil Nos. 1—4, peaty soil Nos. 5—10.

	Dry produce (grams).			Nitrogen, per cent.		Total nitrogen (grams).
	Corn.	Straw.	Total.	Corn.	Straw.	
1. Not inoculated; no lime	9.62	22.12	31.74	3.79	2.40	0.895
2. " " limed.	12.83	22.01	34.84	3.57	2.03	0.905
3. Inoculated; no lime ...	12.16	24.79	36.95	3.58	2.44	1.039
4. " " limed	18.59	28.08	46.67	3.64	1.83	1.190
5. Not inoculated; no lime	1.31	3.04	4.35	3.56	1.64	0.097
6. " " limed.	61.86	67.09	128.95	4.16	1.29	3.439
7. Inoculated; no lime ...	3.44	6.63	10.07	3.45	1.39	0.211
8. " " limed	66.61	83.60	150.21	4.12	1.20	3.744
9. Not inoculated; marled	68.26	82.24	150.50	4.25	1.21	3.900
10. Inoculated; marled....	68.63	90.34	158.97	4.05	1.18	3.845

The roots of the plants of pots 1, 2, 5 had no nodules; those of pots 3 and 7 had very few, whilst in pot 7 there were three agglomerations on one root. On the roots of all the other plants, nodules were more or less abundant.

As regards the experiments in sandy soil, the results show that lime, in the large quantity applied, not only does not injure the nodule bacteria, but considerably assists their development. This is perhaps due, in part, to the strengthening of the plant by the presence of lime during the period in which the bacteria enter the roots. The results obtained with peaty soil clearly indicate the necessity of an application of lime in some form to such soils. The position of the nodules in the pots 6 and 9 indicated accidental inoculation. As in sandy soil, the application of lime did not injure the nodule bacteria.

After the plants were cut, more mineral manure was applied (pots 1 to 4), and pots 2 and 4 received a further application of lime (30 grams each), corresponding with about 48 cwt. per acre, or three times as much as in Salfeld's field experiments (*loc. cit.*), and the quantity of water given was reduced, so as to amount to 10 per cent. of the dry soil. Early in August, field peas were sown. In pots 1 and 3, the plants died, and were re-sown. The following amounts of dry produce and nitrogen were obtained (in grams), including two crops for pots 1 and 3.

Dry produce.				Nitrogen.			
Pot 1.	Pot 2.	Pot 3.	Pot 4.	Pot 1.	Pot 2.	Pot 3.	Pot 4.
7·24	6·05	5·26	15·76	0·299	0·232	0·205	0·573

The results show that even in very dry soil there was no injury to the nodule bacteria by the large application of lime.

The results obtained in the field (*loc. cit.*) still remain, therefore, unexplained. Further experiments are in progress.

N. H. J. M.

Nitrogen Assimilation of some Papilionacæ. By JOHANN BILLWILLER (*Inaug. Diss., Bern., 1895, 50 pp.*).—In the first series of experiments described, lupins, vetches, and peas were grown in sand nearly free from nitrogen, (1) with no nitrogen added, (2) with nitrate, (3, 4, 5, and 6) inoculated from pea nodules, from vetch nodules, from lupin nodules, and with garden soil extract respectively. There were also pots with oats and with buckwheat, with and without nitrate. The necessary ash constituents were supplied in each case. Whilst the oats and buckwheat failed in absence of nitrate, the papilionaceous plants all developed and grew well both with and without nitrate, and also in the pots which had not been inoculated, owing to the sand not having been sterilised. The peas which received nitrate contained 4·223 per cent. of nitrogen, the others 4·318 per cent.

In the second series, there were three pots, each with two peas and one vetch; the first had nitrate, the second and third no nitrate, but the second was subsequently inoculated with a single pea nodule. The sand of all three pots had been sterilised. At the end of the experiment, it was found that the nitrate pot had become accidentally

infected, the plants having nodules on the roots. The following amounts of produce were obtained (grams).

Nitrate; inoculated.		No nitrate; inoculated.		No nitrate; sterilised.	
Peas.	Vetches.	Peas.	Vetches.	Peas.	Vetches.
16.35	10.12	13.5	7.5	1.94	0.65

The third series was similar to the second, and included peas, vetches, and beans, special precautions being taken to avoid accidental infection. Each set comprised several pots; the average results (in grams) were as follows.

	Peas.	Vetches.	Beans.
Inoculated; without nitrate*	10.11	6.7	3.68
Sterilised; with nitrate.....	6.18	2.93	2.98
„ without nitrate...	4.09	1.33	failed

The sterilised plants had roots much more branched and more fibrous than the inoculated plants. Nodule formation was greatest in positions where air had access, as, for instance, near the openings at the bottom of the pots; this is in accordance with the fact that the papilionaceæ grow chiefly on light soils.

Experiments were made in which the same plants (peas, vetches, and beans) were grown in pots filled with rich soil, with and without the addition of calcium carbonate (20 per cent.). The following average amounts of produce were obtained (in grams).

	Peas.	Vetches.	Beans.
With calcium carbonate	20.96	8.85	25.68
Without calcium carbonate..	11.52	7.98	22.50

The peas were thus specially benefited by the application of calcium carbonate.

N. H. J. M.

Effect of Chemical Agents on Germination. By WILHELM SIGMUND (*Landw. Versuchs-Stat.*, 1896, 47, 1—58).—Seeds of wheat, rye, barley, peas, and rape were kept for 24 hours in various solutions, and then left to germinate between moist filter paper. In the case of insoluble, or sparingly soluble, substances, the seeds were placed on a layer of the substance on moist filter paper. The effect of the vapour of volatile liquids was also studied. The exact conditions of temperature, &c., are recorded.

The chemical agents employed were—elements (iodine, sulphur, carbon, zinc, iron, and antimony), oxides, peroxides, acids, bases, salts, hydrocarbons, halogen derivatives, alcohols and ethers, &c.; nitrogen compounds including hydrogen cyanide, potassium ferro-, and ferri-

* In summarising these results, it is stated that the greatest production of organic substance was obtained, in each case, under the influence of *inoculation and with nitrogen*; next without inoculation, but with nitrate; and lastly, without inoculation and without nitrogen. The plan of the experiments, however, as previously stated, was to grow the plants (1), inoculated, but without nitrogen; (2), not inoculated, but with nitrate; and (3), not inoculated, and without nitrate; and the headings of the three tables of results, from which these numbers are taken, are in accordance with this plan.—N. H. J. M.

cyanides, urea; organic acids and salts, tannin, fats, and ethereal oils, pyridine, alkaloïds, substances resembling alkaloïds physiologically (sulphonal, tertiary amylc alcohol, paraldehyde, antipyrine, &c.); antiseptics, and coal-tar dyes. There were 17 series, comprising 275 experiments, including about 200 different substances.

The results show that, as regards acids, both mineral and organic acids are injurious, and that strongly acid salts (such as hydrogen potassium sulphate) are more injurious to germination than the corresponding neutral salts. The different kinds of grain, however, resist, to some extent, the action of acids.

Free bases and strongly basic salts are poisonous. The neutral salts of the alkalis and alkaline earths are without effect, in the case of peas and rape (and probably all *Leguminosæ* and *Crucifereæ*) when the strength does not exceed 0·5 per cent., and sometimes even beneficial up to 0·3 per cent. All other salts are injurious, and generally, when much less concentrated.

Fats and ethereal oils prevent the germination of corn, and very much retard peas and rape.

Anæsthetics and hydrocarbons generally retard germination, whilst their vapours kill the seeds. Peas are the most resistant.

Alkaloïds and similar (physiologically) substances (0·1 per cent.) retard germination more or less. Grain, however, generally developed normally, whilst peas were the most sensitive. Greater concentration is injurious. The organic antiseptics are all injurious in solutions of more than 0·1 per cent.

Coal-tar dyes are poisonous in 0·05 per cent. solutions. (Compare Jarius, *Abstr.*, 1886, 90; Tautphöns, *Bied. Centr.*, 9, 351; Nessler, *ibid.*, 12, 125; Bruttini, *Staz. Sper. Agron.*, 1894, 27 and 30; Mosso, this vol., ii, 326; Haselhoff, *Abstr.*, 1894, ii, 208; 1896, ii, 267; König and Haselhoff, *ibid.*, 1896, ii, 210). N. H. J. M.

Effect of some Substances used as Manures on Germination.

By CLAUDEL and J. CROCHETELLE (*Ann. Agron.*, 1896, 22, 131—142).

—Incrustation of seeds is often practised solely to facilitate their dissemination, although it is frequently asserted that when lime or nutritive substances are employed, the effect on germination is the same as steeping. A number of experiments were made with the view of ascertaining whether certain salts, in small quantities, hinder germination, or are beneficial. In the first series of experiments, now described, the seeds were placed in sand contained in flat dishes, and watered with equal amounts of pure water, and of dilute solutions of the various salts. The seeds selected were sanfoin, lupin, vetch, horse-bean, pea, lentil, lucerne, colza, mustard, flax, and wheat. The manurial substances were: potassium sulphate and chloride, ammonium sulphate, ammonium, potassium, magnesium, and iron phosphates, phosphoric acid, basic slag, lime, chalk, and sodium nitrate. The soluble compounds were used in solutions of various strength (0·05, 0·1, 0·2, and 0·5 per cent.), the insoluble compounds mixed with the sand. The results, which are fully given in tables, showing the numbers of seeds which germinated under the different conditions, show that the potassium salts, ammonium sulphate, sodium nitrate,

and superphosphate, in the quantities applied were injurious to germination, but not on all the seeds equally; wheat being best able to resist their action, lentils, lucerne, and flax being specially sensitive. Lime water and basic phosphates are very favourable to germination, especially in the case of leguminous seeds.

The results of experiments on germination in 0·05, 0·1, 0·2, and 0·5 per cent. sulphuric acid, showed that in the most dilute of the solutions, clover and beet only partially germinate, colza not at all, whilst vetches, wheat, barley, and oats germinate as in water. In 0·1 per cent. acid, oats alone germinated completely (although late); of barley, only 40 per cent. germinated, and of vetches one-third. Wheat, beet, clover, and colza did not germinate. In the stronger solutions (0·2 and 0·5 per cent.), none of the seeds germinated.

The amount of acid produced during the germination of different seeds was next determined. The results are expressed as sulphuric acid per cent. on the weight taken.

Wheat (8 days).....	0·387	Lentil.....	0·304
„ (well germinated)	0·558	Vetch.....	0·273
Oats (8 days) ..	0·186	Pea.....	0·207
Barley	0·285	White lupin	0·465
Rye.....	0·300	Flax	0·108
Colza	0·443	Hemp	0·124
Beet	0·325	Rape.....	0·713
Clover	1·612	Mustard.....	0·452
Horse-beans	0·139	Spurrey.....	0·279

The amount of acid produced is thus very great, and it is thought that the favourable effect of lime, &c., is due to the neutralisation of the acids, and also to the prevention of loss of phosphoric acid or acid phosphates liberated during germination, by forming insoluble phosphates. To the same cause may also be attributed the benefit to acid soils by liming.

It is concluded that an appropriate treatment of seeds is immersion in dilute liquid manure or incrustation with lime.

N. H. J. M.

Formation and Behaviour of the Pentoses in Plants and Animals. By K. GOETZE and THEODOR PFEIFFER (*Landw. Versuchs-Stat.*, 1896, 47, 59—93).—Pentoses are formed in plants from the commencement of their growth, and can be utilised as a reserve substance (like the true carbohydrates) if assimilation is stopped by exclusion of light. The production of pentoses is coincident with that of cellulose, and whether this production has any direct influence on lignification or not, it is noteworthy that it probably always accompanies it.

The *Gramineæ* seem to be particularly rich in pentoses, whilst the *Leguminosæ* contain much less.

Pentoses are partly resorbed and partly rejected by animals. In experiments with sheep, no determinable amount of pentoses was found in the urine, but the greater production of hippuric acid, after the consumption of easily digested pentoses, indicates that some relation exists between the two, and throws light on the results of

Henneberg's metabolism experiments, and on Meissner and Shepard's investigations on the production of hippuric acid in the animal organism.
N. H. J. M.

Combustibility of Tobacco. By ALEXANDER CSERHÁTI (*J. Landw.*, 1895, 43, 379—458).—Nessler's statement that tobacco containing over 0·4 per cent. of chlorine with less than 2·5 per cent. of potash will not burn well, and the view that the combustibility of tobacco depends mainly on the amounts of chlorine and potash it contains, are erroneous. The combustibility varies with the position of the leaves on the stem, the central leaves generally, but not always, burning best. Different varieties of tobacco vary considerably in combustibility, even when grown under exactly the same conditions. The Hungarian varieties mostly burn feebly, owing partly to the soils and partly to the climate; moisture and warmth are favourable to combustibility, which is diminished by a dry climate. As regards soil, the physical properties are of considerable importance. The application of dung in the spring is not always so injurious to combustibility, as is frequently stated. As regards nitrogenous manuring, ammonium sulphate is injurious, whilst sodium nitrate is not. Phosphatic manures are not usually injurious, and sometimes increase the combustibility. Potash is not at all as beneficial as is generally supposed; it has, as a rule, no effect in the case of clay soils. Liming is extremely advantageous in increasing the combustibility of tobacco when the soil is poor in lime (compare Patterson, this vol., ii, 211).

N. H. J. M.

Reduction of Nitrates in Arable Soil. By EMILE BRÉAL (*Ann. Agron.*, 1896, 22, 32—37).—In comparing the effects of sodium nitrate with lucerne (as green manure), bullock's urine, and cow dung (all containing equal amounts of nitrogen), Wagner (*Journ. Agric. Prat.*, 1895, 26 Aug.) found that the most nitrogenous crops were obtained with the nitrate. The nitrogen of the lucerne and of the urine were well utilised when used alone, but when the urine and dung were employed together there was a great loss of nitrogen, which was attributed to denitrification by ferments. In 1892, the author showed the presence of denitrifying ferments in certain vegetable substances, notably in wheat straw (*Abstr.*, 1892, 1259), and evidence is now given showing the effect of denitrification in soils.

Two lots of 200 grams of good soil were watered each with 100 c.c. of well water, and with the same water containing denitrifying organisms from straw. On extracting the soils with equal amounts of water, the following amounts of nitric nitrogen were found: with denitrifying water 0·008, with pure water 0·143 gram. These amounts calculated per hectare represent 4 kilos. and 71·5 kilos. respectively (or about 3·5 and 64 lbs. per acre). When, however, straw is incorporated with the soil, nitrification may be greatly increased, and denitrification more or less checked (compare Deherain and Pagnoul, this vol., ii, 329), owing to the loosening of the soil and the consequent aëration.

The effect of consolidation in inducing denitrification was shown by filling a glass tube, 0·4 metre long, with rich garden soil under-

going vigorous nitrification. After consolidating the soil by tapping the tube, 150 c.c. of water was continually passed through the soil and back again for three weeks. The amount of nitrates in the water rapidly diminished, and at the end of the experiment diphenylamine sulphate no longer gave a coloration.

N. H. J. M.

Causes of Loss of Nitrogen in Decaying Organic Matter, especially Farmyard and Liquid Manure. By R. BURRI, E. HERFELDT, and ALBERT STUTZER (*J. Landw.*, 1895, **43**, 1—11).—Experiments were made with the object of ascertaining how to avoid loss of ammonia in manure by hindering volatilisation of ammonia and by controlling the action of the bacteria which produce ammonia. A nutritive solution was employed containing peptone (1·0), urea (1·0), potassium phosphate (0·1), sodium chloride (0·1), magnesium sulphate (0·05 per cent.), and traces of calcium chloride. In the different experiments, this solution was mixed with an equal volume of water and weighed quantities of the substances to be examined, namely gypsum, superphosphate gypsum, kainite, and dicalcium phosphate; free phosphoric acid was added in a diluted condition. The experiments were made in wide test-tubes with 20 c.c. of liquid, infected with two drops of liquid manure, and kept at 30°. From these infected "original cultivations" small quantities were taken out (after 1 or 24 hours), and added to fresh nutritive solutions without preservatives. In this manner it could be seen whether the bacteria of the original cultivation had been destroyed. Corallin-paper was used to detect ammonium carbonate.

The following conclusions are drawn from the results of the experiments. Gypsum (2·5 to 10 per cent.) is quite useless as a preservative; it neither fixed already formed ammonia nor sufficiently hindered the production of ammonia even when employed in large quantities. Kainite (2·5 to 10 per cent.) hindered ammonia production considerably, but is not an absolutely safe means of preventing loss. Dicalcium phosphate (2·5 to 10 per cent.) is quite useless. Superphosphate gypsum (0·4 to 1 per cent. soluble P_2O_5) and free phosphoric acid (0·4 to 1 per cent.) are both very effective. It is not thought that phosphoric acid has itself any specific action on the ammonic bacteria, but that its action is due to its acid reaction. In one hour, the phosphoric acid killed the bacteria, but did not destroy the spores; in 24 hours, the spores were also destroyed when more than 0·4 per cent. of the acid was added (compare Immendorff, *Abstr.*, 1894, ii, 210).

N. H. J. M.

Manurial Effects of Magnesium Compounds and of Iron Sulphate. By A. LARBALÉTRIER and L. MALPEAUX (*Ann. Agron.*, 1896, **22**, 20—32).—The alleged injurious effect of magnesia on plants seems to be only correct in the case of the chloride, other salts probably being without injury if lime and other fertilising constituents are present in the soil (compare Loew, *Abstr.*, 1895, ii, 206).

A number of experiments are described in which different plants

were grown in sandy soil to which magnesium carbonate and sulphate (each 268 lbs. per acre) and iron sulphate (134 lbs. per acre) respectively were applied, and there was in each case a fourth plot to which nothing had been added. In the case of barley, there was a slight increase of grain and straw under the influence of the magnesium salts (especially the sulphate), but the chief effect was on the weight of the grain, which was, unmanured 46 kilos. per hectolitre, manured with magnesium carbonate and sulphate 49.5 and 50 kilos. respectively. With regard to potatoes, the magnesium sulphate considerably increased the percentage of starch. No very definite conclusions can, however, be drawn from this first series of experiments. It is probable that an application of magnesia to soils containing 0.021 per cent. of magnesia is unnecessary. The sulphate seems to be more active than the carbonate; moreover, the carbonate is somewhat costly, and, owing to its lightness, liable to be lost by winds. It is possible that the application of magnesia along with other salts might be beneficial and remunerative. Further experiments are required.

N. H. J. M.

Effect of Different Amounts of Lime and Magnesia on the Development of Pine Trees. By OSCAR LOEW and SEIROKU HONDA (*Bull. Coll. Agric., Imp. Univ., Tokyo*, 1896, **2**, 378—386).—Whilst calcareous soils are valued for agriculture and forestry, especially for pines, magnesia may be injurious if present in quantity in excess of that of the lime (Wolff, *Landw. Versuchs-Stat.*, **6**, 218; Raumer and Kellerman, *ibid.*, **25**, 31; and Loew, *ibid.*, **41**, 469), although to a much less extent when in the form of the sparingly soluble carbonate.

A number of experiments were made in which young plants of *Cryptomeria japonica*, *Thuja obtusa*, and *Pinus densiflora* were planted in pots containing sand (5 kilos.) which had been thoroughly extracted with strong hydrochloric acid. The plants were watered with a solution containing K_2HPO_4 (1.0), KCl (1.0), $(NH_4)_2SO_4$ (2.0), and $FeSO_4$ (0.1 per cent.), and with varying amounts of (a) 1 per cent. calcium nitrate and (b) 1 per cent. magnesium sulphate solutions, thus: pots 1 to 4 (A) 50, 45, 25, and 10 c.c. of solution (a); pots 2 to 5 (B) 5, 25, 40, and 50 c.c. of solution (b) respectively. The results are given in detail in tables showing the height of the plants after the first and second years, number of branches, total weight, &c., and there are also photographs of the plants of the two series.

The results point to the conclusion that a calcareous soil is favourable to the growth of pines when the amount of magnesia is relatively very small, but becomes less favourable when the magnesia is in excess of the lime. The effect of deficiency of lime is most conspicuous in producing short needles.

N. H. J. M.

Analytical Chemistry.

Volumetric Analysis of a Mixture of Chlorides, Hypochlorites, and Chlorates. By ADOLPHE CARNOT (*Compt. rend.*, 1896, **122**, 449—452).—The hypochlorite is first estimated by means of a standard arsenite solution. The liquid is then acidified, mixed with ferrous ammonium sulphate equal to at least 20 times the weight of the chlorate supposed to be present, boiled out of contact with air, and gradually mixed with 5 c.c. of sulphuric acid diluted with 15 c.c. of water. The excess of ferrous salt is determined with permanganate solution, and the amount of chlorate is thus ascertained. An aliquot part of the liquid is mixed with a few drops of ferrous sulphate to remove excess of permanganate, an excess of a standard solution of silver nitrate is then added, and the silver remaining in solution is estimated by thiocyanate solution. The total chlorine is thus determined.

C. H. B.

Analysis of a Mixture of Chlorides, Chlorates, and Perchlorates. By ADOLPHE CARNOT (*Compt. rend.*, 1896, **122**, 452—454).—The chloride may first be estimated by means of silver nitrate and thiocyanate solutions; the chlorate is then reduced by means of ferrous sulphate (preceding abstract), and the chlorine again determined in the same way. The ferrous sulphate does not reduce perchlorates.

Another plan is to estimate the chloride directly with silver nitrate solution, using an alkali arsenate as indicator, and then estimate the chlorate by means of ferrous sulphate (*loc. cit.*).

In order to estimate the perchlorate without loss by volatilisation, the solid substance is mixed with four or five times its weight of well washed and dry quartz sand. This mixture is placed in a platinum crucible and covered with a layer of the sand to a depth of 1 to 2 cm.; the crucible is then heated for 20 or 30 minutes with a Bunsen flame in such a way that only the bottom of the crucible becomes red hot. No chlorine is lost, and the total chlorine in the residue is estimated by means of silver nitrate solution.

C. H. B.

Detection of Fluorine in Beer. By J. BRAND (*Chem. Centr.*, 1895, ii, 906; from *Zeit. ges. Brauw.*, **18**, 317—319).—One hundred c.c. of the sample is rendered alkaline with ammonium carbonate, heated to boiling and precipitated with 2—3 c.c. of a 10 per cent. solution of calcium chloride. The precipitate is collected on a filter, slightly washed, and calcined in a 25 c.c. platinum crucible, 1 c.c. of sulphuric acid is added, and hydrogen fluoride tested for in the well-known way by its action on glass. The heating is continued for an hour, the top of the watch-glass being cooled with ice. The presence of 0.01 gram of ammonium fluoride in a litre of beer may thus be detected.

L. DE K.

New Process for estimating Sulphur in Organic Compounds. By ALEXANDER VON ASBÖTH (*Chem. Zeit.*, 1895, 19, 2040).

—The author's process may be used when the substance is not too volatile. One gram of the powdered sample is mixed in a nickel crucible with 10 grams of dry sodium carbonate and 5 grams of sodium peroxide, and then very gradually heated to complete fusion. The mass, after cooling, is dissolved in water, and the solution is filtered; and after acidifying with hydrochloric acid containing bromine, and boiling, the sulphuric acid is precipitated with barium chloride.

The process is also suitable for liquids or extracts; these are first evaporated with 5 grams of sodium carbonate, another 5 grams of the latter and 5 grams of the peroxide is then added, and the mixture is fused.

L. DE K.

Estimation of Citrate Soluble Phosphoric acid in Basic Slags. By PAUL WAGNER (*Chem. Zeit.*, 1895, 19, 1419—1421).

—Five grams of the finely powdered sample is introduced into a special half-litre flask which is filled up to the mark with solution of ammonium citrate; the flask is then fixed in a rotating apparatus turning round its axis 30—40 times per minute. The citrate solution is made by dissolving 150 grams of pure citric acid in water, adding a quantity of ammonia containing exactly 27.93 grams of NH_3 , and then making up to 1 litre; before use, two volumes of this liquid is diluted with three volumes of water.

After the shaking, the liquid is filtered, and 50 c.c. is mixed with solution of ammonium molybdate, and heated for 10—15 minutes in a water bath at 80—95°. The molybdate is best prepared by dissolving 125 grams of the acid in 100 c.c. of water and 300 c.c. of 8 per cent. ammonia; after adding 400 grams of ammonium nitrate, the mixture is made up to a litre, poured into a litre of nitric acid of 1.19 sp. gr., kept at 35° for 24 hours, and then filtered. The yellow phosphate precipitate is first washed with water containing 1 per cent. of nitric acid, and then dissolved in 100 c.c. of cold 2 per cent. ammonia; 15 c.c. of magnesia mixture is now slowly added, and, after two hours, the precipitate is collected, washed with ammonia of 2 per cent. strength, and then treated as usual.

The author prepares the magnesia mixture by dissolving 110 grams of crystallised magnesium chloride and 140 grams of ammonium chloride in 700 c.c. of 8 per cent. ammonia and 1300 c.c. of water.

L. DE K.

Estimation of Arsenic. By RODOLPHE ENGEL and J. BERNARD (*Compt. rend.*, 1896, 122, 390—392).

—Oxygen compounds of arsenic are completely reduced by hypophosphorous acid in presence of concentrated hydrochloric acid, and the reduced arsenic is attacked by iodine with formation of arsenious acid in acid solutions, and arsenic acid in presence of alkalis. The arsenic solution is concentrated to 20—40 c.c., mixed with three times its volume of hydrochloric acid of 22° B., and a large excess of hypophosphorous acid. After remaining for about 12 hours in a well closed vessel, the liquid is heated gently on a water bath, mixed with an equal volume of boiled and still boiling water, filtered, and the precipitate well washed with

boiling water. The precipitate is then gradually mixed with a decinormal solution of iodine until the liquid is no longer decolorised after waiting for 2 or 3 minutes; 50 c.c. of water and 10 c.c. of a saturated solution of sodium hydrogen carbonate are then added, and the titration is completed, using starch as indicator; 1 c.c. of the decinormal iodine solution represents 0.0015 gram of arsenic.

The analyses quoted in the paper indicate that the method gives good results in presence of nickel, cobalt, manganese, aluminium, and zinc.
C. H. B.

Estimation of Arsenic. By E. J. ARMAND GAUTIER (*Compt. rend.*, 1896, 122, 426—427).—The author points out that the method of weighing the ring of metal deposited in Marsh's method is especially applicable to the detection and estimation of very small quantities of arsenic or antimony, and that the results are accurate even with so little as 2 milligrams of arsenic.
C. H. B.

Volumetric Estimation of Boric acid. By GUNNER JÖRGENSEN (*Chem. Centr.*, 1895, ii, 803; from *Nordisk. pharm. Tidsskr.*).—To estimate boric acid in articles of food, milk for instance, 100 c.c. of the sample is mixed with a little sodium carbonate, evaporated to dryness, incinerated, and the ash dissolved in dilute nitric acid; the liquid is then filtered and heated to expel carbonic anhydride. Aqueous soda is now added until the liquid is neutral to phenolphthaleïn; some glycerol is next added, and the boric acid titrated with normal soda; 62 grams of boric acid require for neutralisation 1014 c.c. of normal alkali.
L. DE K.

Estimation of Carbon in Iron. By PEIPERS (*Chem. Centr.*, 1895, ii, 803; from *Österr. Zeit. Berg-Hütt.*, 34, 477—478).—For the estimation there are required two unglazed porcelain slabs, a beaker containing a 12.5 per cent. solution of ammonium cupric chloride, and six standard samples of steel containing from 0.2—1.2 per cent. of carbon. Streaks are made on the porcelain slabs with the sample and with the standard samples, and they are then immersed in the copper solution for a few minutes. The iron dissolves, and only leaves the carbon marks, which are then compared as to their intensity.
L. DE K.

A new Apparatus for estimating Carbon. By F. WÜST (*Chem. Centr.*, 1895, i, 1189; from *Stahl u. Eisen*, 15/1, 389—390).—A very elaborate apparatus is used, which, however, will reduce errors to a minimum. The oxidation of the carbon is effected by boiling with sulphuric and chromic acids, and the undue evaporation of sulphuric acid is prevented by introducing into the evolution flask a cooling arrangement. The gas passes through a specially constructed U-tube filled with glass beads moistened with sulphuric acid and then through a combustion tube filled with copper oxide, and heated to redness; to prevent burning of the rubber joints, the ends of the tube are kept cold by a special water-flow arrangement. The carbonic anhydride is again dried by means of glacial phosphoric acid, and then absorbed in two weighed soda-lime tubes containing also some glacial phos-

phoric acid; a sulphuric acid guard tube is provided, and also an arrangement for drawing purified air through the apparatus.

L. DE K.

Separation of Calcium from Strontium and Barium. By J. DUPASQUIER (*Bull. Soc. Chim.*, 1895, [3], 13, 678—681).—Calcium in the form of a soluble salt, or as the sulphate, is completely transformed into the tartrate on treatment with a solution of an alkali hydrogen tartrate containing a soluble sulphate. The soluble salts of barium and strontium are, however, under the same conditions converted into insoluble sulphates. The separation is, therefore, easy, the calcium tartrate being readily soluble in dilute mineral acids.

When both calcium, barium, and strontium are present, a measured quantity of the hydrogen tartrate and sulphate solution is added (the quantity of sulphate present being known); the calcium is then separated as above, and the relative proportions of strontium and barium deduced from the weights of the combined sulphates and the quantity of unchanged sulphate in the filtrate.

J. F. T.

Estimation of Zinc in Dried Apples. By LUDWIG LEGLER (*Chem. Zeit.*, 1895, 19, 1763).—Fifty grams of the sample, dried in a porcelain basin, is completely charred, and the residue powdered and boiled with hydrochloric acid; after diluting and filtering, excess of ammonia is added and the liquid diluted to a convenient bulk. An aliquot part of the clear solution is then acidified with acetic acid, and any zinc is precipitated with hydrogen sulphide. If, to save time, the charred portion is not filtered off before adding the ammonia, a slight correction for volume must be made. The author finds that it generally occupies 3 c.c.

L. DE K.

Estimation of Copper by precipitating with Sodium Thio-sulphate and heating to Oxide. By H. NISSENSON and B. NEUMANN (*Chem. Zeit.*, 1895, 19, 1591—1592).—The authors have found that the cuprous sulphide obtained by boiling a hydrochloric acid solution of a copper salt with sodium thiosulphate is readily and completely converted into oxide by ignition in a muffle, and recommend this process for the commercial assay of copper ores and compounds.

Arsenic comes down to some extent, but is completely expelled on ignition. Cadmium does not interfere. Large quantities of tin, antimony, lead, &c., must first be removed by the usual methods.

L. DE K.

The Iodide Assay for Copper. By Low (*Chem. Centr.*, 1895, ii, 64; from *Eng. Min. J.*, 1895, 9/2).—The ore is dissolved in nitric acid, boiled with hydrochloric acid, and evaporated with sulphuric acid; the residue is then dissolved in water and filtered from any lead sulphate. The copper in the filtrate is precipitated by boiling with a sheet of aluminium, washed by decantation, and dissolved in a few c.c. of nitric acid; after fully oxidising any arsenic by means of a little potassium chlorate, the liquid is boiled, mixed with excess of ammonia, then strongly acidified with acetic acid, and the copper titrated, as usual, with potassium iodide and sodium thiosulphate.

The latter solution is standardised by means of metallic copper, also in acetic acid solution. L. DE K.

Estimation of Alum in Wines. By GEORGES (*Bull. Soc. Chim.*, 1895, [3], 13, 692—696).—This method depends on (1) the properties of aluminium gallotannate, (2) the fact that natural red wines and those which have been adulterated with alum behave differently on the addition of ammonium acetate or of neutral sodium acetate in the presence of a small quantity of tannin (from nut galls).

Alluminium gallotannate is precipitated from a solution of tannin by means of aluminium acetate in the form of a white, voluminous precipitate. It is readily soluble in strong acids; dilute acetic acid is without action on it; decinormal solutions of potassium or sodium hydroxides dissolve it readily in the cold.

The necessary solutions for the estimation are (1) a solution of tannin containing 3.40 grams in 100 c.c. of water, (2) a solution of crystalline neutral sodium acetate containing 24 grams in 100 c.c. of water. 20 c.c. of the wine is placed in a test-tube, and 2 c.c. of the tannin solution added; after shaking, 3 c.c. of the acetate solution is poured into the tube. If, after five minutes, a flocculent precipitate is formed, the wine is adulterated (that is, contains more than 0.1 gram of alum per litre); if, however, the solution remains clear, or becomes only slightly opaque, the wine is natural.

If it is required to estimate the alum present, 500 c.c. of the wine is taken, and a volume of the solutions corresponding with 1 gram of tannin, and 25 grams of sodium acetate added; the precipitate is then collected, ignited, and weighed as alumina. J. F. T.

Detection of Cobalt by Nitroso- β -naphthol. By MICHAEL VON ILINSKI (*Chem. Zeit.*, 1895, 19, 1421).—The test is best carried out by adding to the solution to be tested an acetic acid solution of nitroso- β -naphthol; on heating, a voluminous, dark red precipitate is formed. To guard against the separation of nitroso- β -naphthol, which may be mistaken by the inexperienced for the cobaltic compound, the author recommends adding an equal bulk of alcohol.

Traces of cobalt are best detected by omitting the alcohol and adding a cold aqueous solution of the reagent. It is necessary that the cobalt solution should contain free hydrochloric acid, also that the reagents should be freshly prepared. The test works well in the presence of nickel. L. DE K.

Analysis of Tin Slag. By HENRY BAILEY (*Chem. News*, 1896, 73, 88).—Tin slag consists chiefly of double silicate of iron and aluminium with some stannous silicate, shots of metal, small quantities of lime, tungsten, &c., and, occasionally, unreduced stannic oxide. The iron, tin, and silica are usually estimated, and for this purpose the following method is suggested: 2 grams of the finely pulverised slag is evaporated with 10 c.c. of fuming nitric acid until nitrous fumes cease to be evolved; it is then boiled for some time with 20 c.c. of strong hydrochloric acid, diluted with an equal bulk of water, reduced with zinc, filtered, and washed. The iron in the filtrate is estimated by means of potassium dichromate. The washed residue

is warmed with 10 c.c. of hydrochloric acid and a few drops of nitric acid, to oxidise any tungsten, diluted, filtered, washed with boiling water, and the warm filtrate and washings treated with hydrogen sulphide; it is then left to settle in a warm place, collected, washed, dried, ignited, and weighed as stannic oxide. The silica is washed with dilute ammonia, subsequently with water, dried, ignited, and weighed; by evaporating and igniting the ammoniacal washings in a platinum dish, and weighing the tungsten oxide, an idea of the amount of tungsten present is obtained. To estimate alumina, the solution containing the iron and alumina is nearly neutralised with sodium carbonate and boiled with 10 grams of sodium thio sulphate until the odour of sulphurous anhydride has disappeared. The precipitate is washed, dried, ignited, and weighed, and the solution is acidified with hydrochloric acid, boiled until free from sulphurous anhydride, and then titrated with standard dichromate.

D. A. L.

Testing Petroleum by Fractional Distillation. By RICHARD KISSLING (*Chem. Zeit.*, 1895, 19, 1227).—The author, in reply to Engler, states that his own apparatus gives constant results, and shows small differences in the composition of the samples. This cannot be said of Engler's distillation apparatus.

L. DE K.

Detection of Paraffin in Olive Oil. By E. CARPENTIER (*Chem. Centr.*, 1895, ii, 664; from *Bull. l'Assoc. Belge Chim.*, 1895, 75).—Saponification and agitation of the soap solution with ether is impracticable, as a firm emulsion is obtained. For a quantitative estimation, 10 grams of the oil is saponified with alcoholic soda, and the solution evaporated to dryness at 80–90°. The residue is then rubbed with sand and extracted in a Soxhlet apparatus with light petroleum.

If a qualitative test only is desired, the soap solution is decomposed by an acid, and the mixture of fatty acids and paraffin is filtered off. This is then dissolved in alcohol, carefully neutralised with alcoholic potash, and diluted with water. If paraffin is present, the solution will become turbid.

L. DE K.

Estimation of Oil of Mustard. By OTTO FOERSTER (*Chem. Zeit.*, 1895, 19, 2002).—The author states that his method of estimating the sulphur in oil of mustard by means of ammonia and mercuric oxide, and weighing the resulting mercuric sulphide, is preferable to the alkaline permanganate process proposed by Schlicht. It is admitted, however, that the results are only approximate.

L. DE K.

Assay of Glycerol for the Manufacture of Dynamite. By JULIUS LEWKOWITSCH (*Chem. Zeit.*, 1895, 19, 1423–1425).—The sample should be fairly pure, as impurities constitute a source of danger. The sp. gr. should not be less than 1.261 at 15.5°. Lime, magnesia, and alumina should be absent. Chlorine or arsenic should not exceed a trace. Organic acids and other organic matter should be absent.

A sample which passes all these tests may still be unfit for manufacturing nitroglycerol, and a practical test should therefore be made.

The nitro-product should readily and completely separate from the acid, and may then be measured. The yield should be at least 207—210 per cent.; 246·7 per cent. is the theoretical quantity. The author gives a number of precautions to be observed when making the practical test, which should only be attempted by an experienced operator.

L. DE K.

Estimation of Water in Raw Sugars. By JAN W. GUNNING (*Chem. Centr.*, 1895, ii, 948; from *Sucrierie Belge*, 23, 180).—One hundred grams of the sample of beetroot sugar is dried for five hours at 108°; the drying is attended with a very slight decomposition, and about 0·1 per cent. of the loss is caused by carbonic anhydride and traces of volatile bases. When drying raw cane-sugar, the fatty acids contained therein cause a slight inversion and also partial destruction of the levulose, which also happens if the sample is heated out of contact with oxygen.

L. DE K.

Estimation of Pentoses and Pentosans by means of the Furfuraldehyde Reaction. By A. STIFT (*Chem. Centr.*, 1895, ii, 67; from *Österr.-ung. Zeit. Zucker-Ind.*, 24, 290—294; compare this vol., ii, 79).—The estimation of furfuraldehyde in molasses and osmose waters is very difficult, on account of the persistent foaming during the distillation with hydrochloric acid, and the incomplete precipitation of the distillate by phenylhydrazine acetate.

The precipitate should be dried in a vacuum. Multiplication by 2·09 and 1·84 gives respectively the pentose or pentosan number.

L. DE K.

Behaviour of Sugars towards Alkaline Copper Solution. By JOHAN G. C. T. KJELDAHL (*Chem. Centr.*, 1895, ii, 665; from *Carlsberg. Lab. Meddelser.*, 1895, 4).—The author states that the quantity of copper precipitated from Fehling's solution by glucose is seriously diminished by free access of air. Experiments were made with narrow-necked flasks, a beaker, a deep basin, and a very flat dish; by using the latter, a loss of nearly 0·02 gram of copper was caused. Trustworthy results can only be obtained by working in a current of hydrogen.

The products of oxidation of the sugar are, besides formic acid, glycollic acid, glyceric acid, trihydroxybutyric acid, arabonic acid, and gluconic acid. It is a curious fact that glucose and fructose, when boiled with Ost's copper solution, precipitate about twice as much copper as from Fehling's solution.

L. DE K.

Estimation of Sugars by means of Copper-potassium Carbonate. By HERMANN OST (*Chem. Zeit.*, 1895, 19, 1784—1785, 1829—1830).—Instead of Fehling's solution, the author uses a liquid prepared by dissolving 17·5 grams of copper sulphate in water, and pouring this slowly into a solution of 250 grams of pure potassium carbonate and 100 grams of potassium hydrogen carbonate. The solution is then made up to a litre. In some cases, it is advisable to reduce the amount of copper sulphate to 3·6 grams. These solutions are said to keep better than the Fehling liquid, but, as they are

reduced by much less sugar, the author's tables should be consulted. These include the reducing powers of dextrose, levulose, maltose, and mixtures of invert and cane sugar. Cane sugar is said to be scarcely affected by the new solution. If the sugar solution contains traces of lead or calcium, these must be first removed by ammonium oxalate.

L. DE K.

Behaviour of Basic Lead Acetate towards Sugar Solutions.

By HANNO SVOBODA (*Zeit. Ver. Rübenzucker-Ind. Deut. Reichs.*, 1896, 46, Heft 481).—See this vol., i, 406.

Estimation of the Acidity of some Pyroligneous Products.

By AUGUSTE SCHEURER-KESTNER (*Compt. rend.*, 1896, 122, 619—621).—Crude pyrolignic acid, made by distilling wood in closed vessels, contains, amongst other products, methylic acetate; the quantity of this can be ascertained by first titrating the solution with sodium hydroxide in the cold, then adding excess, and boiling for some hours. On titrating back, the difference in the two results gives the quantity of methylic acetate and similar products present. The author also describes a method of titration in the presence of phenols.

J. F. T.

Oxalic acid and Putrefaction. By DIOSCORIDE VITALI (*L'Orosi*, 1895, 18, 304—307).—The possible contingency that oxalic acid used as a poison may undergo change during the putrefaction following death and thus escape detection does not seem to have been considered by toxicologists. On allowing a mixture of water with 100 grams of meat, the white of one egg, and 2 grams of oxalic acid to remain for nine months, putrefaction seemed to be appreciably retarded, but the greater part of the oxalic acid could still be detected in the ordinary way.

W. J. P.

Improvement on Hübl's Chloro-iodine Process. By WALLER (*Chem. Zeit.*, 1895, 19, 1786—1787; 1831—1832).—The paper deals at great length with the theory of the Hübl's solution. As is well known, this reagent rapidly deteriorates in strength; by the author's new way of preparing it, it may be kept at nearly full strength for two months.

Twenty-five grams of iodine is dissolved in 250 c.c. of 95 per cent. alcohol, a solution of 25 grams of mercuric chloride in 200 c.c. of alcohol is added, then 25 grams of hydrochloric acid of 1.19 sp. gr., and the whole is made up with alcohol to 500 c.c., being, therefore, double the strength of the ordinary Hübl solution.

L. DE K.

Testing Vegetable Oils and Butter. By P. LEVIN (*Chem. Zeit.*, 1895, 19, 1832—1833).—An attack on Schönvogel's borax process. Borax is of no use for the detection of vegetable oils in butter, as the emulsion will always form if fatty acids are present. Rancid butter, when tested with borax solution, appears adulterated, whilst some vegetable fats give no emulsion at all.

L. DE K.

Estimation of the Acetyl Numbers of Lard, Cotton-seed Oil, and Tallow. By ED. SPAETH (*Chem. Centr.*, 1895, ii, 623; from

Forsch.-Ber. Lebensm., **2**, 226—227).—The author has taken the acetyl numbers of three kinds of lard, two specimens of cotton-seed oil, and a sample of tallow, also of a mixture of lard with cotton-seed oil and tallow, and has tabulated the results.

The conclusion drawn is that for the detection of cotton-seed oil the process gives no better result than the iodine absorption process.

L. DE K.

Testing of Lard. By H. VOGEL (*Chem. Centr.*, 1895, ii, 845; from *Apoth. Zeit.*, **10**, 633—634).—Lard is often adulterated with cotton-seed oil and tallow, and, with care, mixtures can be made which defeat most of the recognised tests. The best results are obtained by testing the liquid fatty acids. 50 c.c. of the sample is saponified, and the fatty acids are dissolved in 250 grams of carbon bisulphide and 8—10 grams of zinc oxide. The zinc salts of the solid fatty acids are deposited, and those of the liquid acids remain in solution. The carbon bisulphide is distilled off, and the residue is decomposed with hydrochloric acid. The liberated oleic acid is finally tested in the oleorefractometer at 45°, when the deviation should be -30, or it may be titrated; 1 gram should neutralise 0.190—0.191 gram of potassium hydroxide.

L. DE K.

Analysis of Lard and similar Fats. Detection of Vegetable Oils. By FERDINAND JEAN (*Bull. Soc. Chim.*, 1895, [3], **13**, 780—784).—The determination of the refractive index both of the original substance, and of the liquid fatty acids obtained from it, the iodine absorption of the liquid fatty acids, and the quantity of potassium hydroxide necessary to neutralise 1 gram of these acids, yield data from which the presence or absence of vegetable oils can readily be inferred.

A refractive index less than -12.5° (at 45°) for the crude substance, and less than -30° for the liquid fatty acids obtained therefrom, together with a quantity of potassium hydroxide less than 0.0190 gram being required, is, in the author's opinion, sufficient evidence of the presence of vegetable oils.

J. F. T.

Detection of Cotton-seed Oil in American Lards. By J. DUPONT (*Bull. Soc. Chim.*, 1895, [3], **13**, 775—780).—The figures usually taken as representative of a pure sample of European lard are the following: Index of refraction, -12.5°; iodine absorption, 59; action on silver nitrate, none; any figures higher than these being supposed to indicate the presence of cotton-seed oil.

The author has determined the index of refraction and the iodine absorption of the following samples of American lard:—I, leaf lard; II, back lard; III, belly lard; IV, head lard; V, foot lard; VI, gut lard; VII, rancid lard; VIII, sour lard; IX, a sample taken at hazard from the boilers; X, lard oil (Wilcox); XI, lard oil (John Morrell).

	I.	II.	III.	IV.	V.	VI.
Index of refraction..	-11.5°	-5°	-7°	-7°	-4°	-11°
I absorption	58	61	62	63	65	60

	VII.	VIII.	IX.	X.	XI.
Index of refraction	-7°	-6.5°	-7°	-1°	0°
I absorption	63	64	63	80	82

The action of the free acids on silver nitrate solution was in every case negative, Nos. VII and VIII only being somewhat doubtful.

It is, therefore, concluded that the figures usually taken as representative of a pure French lard cannot be applied to samples of American lard, owing to the difference in race and nourishment of the animals and in the mode of preparation of the product.

J. F. T.

Rapid Estimation of Wax-substitute in Bees-wax. By GEORG BUCHNER (*Chem. Zeit.*, 1895, **19**, 1422).—The well-known Hübl test for wax may be defeated by using a judiciously made mixture of stearic acid or resin, with stearin, or japan-wax and paraffin, or ceresin. These mixtures, which can be readily detected qualitatively, all yield to alcohol a large amount of soluble matter of an acid nature, whilst pure wax only gives a small amount of cerotic acid.

Five grams of the suspected sample is boiled with 100 c.c. of 80 per cent. alcohol for five minutes. After cooling, the loss caused by evaporation is carefully restored by adding more alcohol, and the liquid is then filtered. 50 c.c. of the filtrate is titrated with N/10 potash, using phenolphthaleïn as indicator. If the calculated acidity number does not exceed 4.1, the wax may be considered pure; any considerable excess may be put down to the presence of a substitute. As the nature of the latter is known by a qualitative analysis, the amount may be readily calculated by referring to the author's tables. For instance, a mixture of stearic acid, stearin, and ceresin which, by the Hübl test, would appear to be pure wax, has an acidity number of 21.4; a mixture containing resin instead of stearic acid has an acidity number of 22.

L. DE K.

Testing Acetone. By HUGO SCHWEITZER and EMIL E. LUNGWITZ (*Chem. Zeit.*, 1895, **19**, 1384).—To test acetone for water, the authors recommend adding to 50 c.c. of the sample 50 c.c. of light petroleum (boiling point 40—60°). If water is present, two distinct layers will be visible. The reaction is not, however, a quantitative one, as the aqueous layer does not consist of pure water.

In the absence of water, a perfectly clear mixture is obtained.

L. DE K.

Volumetric Estimation of Antipyrine. By M. C. SCHUYTEN (*Chem. Zeit.*, 1895, **19**, 1786).—Antipyrine may be titrated by adding N/50 iodine solution to an aqueous solution of 0.01—0.05 gram of the sample in 1000 times its weight of water, until the liquid turns permanently yellow. The iodine should be added slowly, and no more of it should be added unless the yellow colour has completely disappeared. The reaction is finished if, after one hour, the liquid is still visibly yellow. It is as well to do a blank experiment side by side with pure water. Starch is not to be recommended as indicator in this case. 1 part of iodine represents 1.45 part of antipyrine.

L. DE K.

General and Physical Chemistry.

Reversal of the Double Refraction of Gelatin producing Tissues by Various Reagents. By VICTOR VON EBNER (*Monatsh.*, 1896, 17, 121—125).—The author has previously shown that the double refraction of such colloidal substances as connective tissue, cartilage, decalcified bones and teeth, cornea of the eye, capsule of the crystalline lens, elastic tissue, chitin and spongin, is reversed, that is, changed from positive to negative, or *vice versâ*, when the substances are treated with phenol. Muscle, horny tissue, silk, cellulose, wood, cork, starch, exhibit no such change. It has also been shown that other phenolic substances have a similar power, but neither inorganic nor aliphatic compounds.

The action of various other organic compounds on longitudinal sections of decalcified bone has been studied. Pure aniline, eugenol, carvacrol, orthocresol, guaiacol, all change the positive double refraction to negative. Salicylaldehyde has the greatest action of all, and induces a negative double refraction far greater than the original positive. Crotonaldehyde and citronelaldehyde, propaldehyde and isovaleraldehyde, ethylic acetoacetate, geraniol, menthylic valerate and bornylic acetate have no action. J. J. S.

Argon. By SIEGFRIED FRIEDLÄNDER (*Zeit. physikal. Chem.*, 1896, 19, 657—667).—The author has examined the spectrum of argon as prepared by Guntz's method (*Abstr.*, 1895, ii, 347), and gives the wave-length and intensity in the case of 106 lines which he has observed and measured. Of these, however, 33 seemed coincident with mercury, sodium, lithium, nitrogen, or hydrogen lines, and these disappeared by further sparking, with the exception of an apparent N line at $\lambda = 420\mu$, which is hence probably a true argon line, so that 74 lines due to argon still remain. By continuing the induction sparks "electric vaporisation" of the platinum was observed, while the number and intensity of the argon lines decreased, and ultimately all disappeared, the D_3 helium line being finally visible for a few seconds. It hence appears that by the continued action of the electric discharge argon combines with platinum (compare Troost and Ouyard, this vol., ii, 99). Helium also is present in atmospheric air, but probably not to a greater extent than $1/10^9$, and it also combines with platinum under the above conditions (compare Brauner, *Abstr.*, 1895, ii, 347). A list of 11 almost coincident lines of helium and argon is given, the helium wave-lengths being taken from Runge and Paschen's measurements (this vol., ii, 1). The similarity of the spectra of the two gases is, the author considers, a probable indication of their chemical similarity, so that argon, like helium (this vol., ii, 1), probably consists of two elements, a view he considers further supported by the *simultaneous* dual spectrum of argon (this vol., ii, 104).

L. M. J.

Absorption Spectra of Iodine and Bromine Solutions above the Critical Temperature of the Solvent. By R. W. WOOD (*Zeit. physikal. Chem.*, 1896, **19**, 689—695).—The absorption spectrum of a solution of iodine in carbon bisulphide consists of two bands, red and violet, whilst that of gaseous iodine consists of a number of fine lines. Solutions of iodine in varying quantities of carbon bisulphide were heated in closed tubes to above 300° , and the concentration of the iodine varied until the line spectra became visible, at which point the density of the carbon bisulphide vapour and concentration of the iodine were calculated. These values being represented graphically yield a curve consisting of two straight lines, but similar experiments with bromine gave a curve concave to the axis of bromine concentration. The ratio of the bromine to iodine content at similar solvent density, varied from 6.1 to 9.4, and increased with the concentration. The results are, as the author points out, analogous to those obtained by Haunay and Hogarth for solutions of solids, at temperatures above the critical temperature of the solvent (*Proc. Roy. Soc.*, 1880, **30**, 178 and 484). L. M. J.

Optical Superposition of Six Asymmetric Carbon Atoms in the same Active Molecule. By PHILIPPE A. GUYE and CHARLES GOUDET (*Compt. rend.*, 1896, **122**, 932—934).—Determinations of the rotatory powers of three active amylic tartrates confirm Walden's results, and his conclusion that the total effect of the four asymmetric carbon atoms is the algebraic sum of their separate effects.

Consideration of the extended formula of amylic divaleryl tartrate shows that it contains six asymmetric carbon atoms in three pairs. If prepared (1) from constituents all of which are inactive except the amyl radicle, the compound should have the optical effect of the pair of asymmetric carbons in the two $\text{COO}\cdot\text{CHMeEt}$ groups, symmetrically disposed at the end of the main chain; if (2) from racemic tartaric acid, racemic amylic alcohol, and active valeric chloride, it should have the rotatory power of the central pair of carbons; whilst if prepared (3) from active tartaric acid, all the other constituents being inactive, the rotatory power should represent the effect of the pair of carbons in the other $\text{COO}\cdot\text{CHMeEt}$ groups disposed laterally and unsymmetrically with respect to the main chain. A fourth modification, prepared from wholly active constituents, should have a rotatory power equal to the sum of the other three.

Ethereal salt.	Sp. gr.	Molecular refraction.		Rotatory power, $[\alpha]_D$.
		Observed.	Calculated.	
1	1.0095	119.84	120.05	+2.44
2	1.0066	120.09	120.05	+3.48
3	1.0172	119.06	120.05	+6.42
4	1.0089	119.96	120.05	+11.32

It will be seen that the rotatory power of No. 4 is practically equal to the sum of the rotatory powers of the other three, and this result affords a further and remarkable proof of the independence and the

algebraic superposition of the optical effects of different asymmetric carbon atoms in one and the same optically active molecule.

C. H. B.

Rotatory Dispersion of Non-polymerised Optically Active Liquids. By PHILIPPE A. GUYE and CHARLES JORDAN (*Compt. rend.*, 1896, **122**, 883—886).—As a rule, the rotatory power of a substance for different rays of the spectrum increases with the refrangibility of the rays; this is *normal rotatory dispersion*. With some substances, however, the rotatory power may have opposite signs with different rays, or, whilst retaining the same sign throughout the spectrum, may show a maximum at some particular point; either of these cases is *abnormal rotatory dispersion*.

The authors have measured, by Landolt's method (Abstr., 1895, ii, 1), the rotatory power for different rays of some 13 substances, including a hydrocarbon, a halogen derivative of a hydrocarbon, ethereal salts, and amines, all of them being free from molecular polymerisation as defined by Ramsay and Shields. Tables are given showing (1) the observed rotatory powers for red, yellow, green, blue, and violet; (2) the coefficients of rotatory dispersion, or the ratio of the rotatory power for the particular ray to the rotatory power for red; and (3) the specific rotatory power, the specific dispersion, and the specific rotatory dispersion, the latter being the difference between the specific rotatory powers for red and violet respectively.

The general conclusions are: (1) the non-polymerised optically active liquids show only normal rotatory dispersion; (2) each active compound has its own law of rotatory dispersion; (3) the coefficients of dispersion in the violet have no relation whatever to the magnitude of the rotatory power; (4) whilst the specific rotatory dispersion is not proportional to the specific rotatory power, the order of magnitude of the two quantities generally varies in the same direction; (5) the specific rotatory dispersion, like the specific rotatory power, is a characteristic constant of a chemical compound; (6) there is no simple relation between the refractive effect on different rays and the rotatory dispersion.

C. H. B.

Photochemistry and Thermophotochemistry. By RODOLFO NAMIAS (*Gazzetta*, 1896, **26**, i, 35—52).—The author discusses at length the various chemical changes attending photographic action. Although light can cause both endothermic and exothermic reactions to occur, the former only proceed, as a rule, to a very slight extent, owing to the reverse exothermic reaction setting in between the decomposition products. The usefulness of chemical sensitisers is due to their being able to react exothermally with certain of the decomposition products, and so facilitate the photographic action. In exothermic reactions, the light acts merely as an exciting agent, but in endothermic reactions it plays the part of a source of energy; all endothermic photographic reactions cease when the light ceases to act, and those reactions which continue in the dark after cessation of the light action must be exothermic.

W. J. P.

The Potential Difference between Gases and Liquids. By FRANK B. KENRICK (*Zeit. physikal. Chem.*, 1896, **19**, 625—656).—A difference of potential has been proved to exist at the surface of separation of gases and liquids, and drops of water falling through, receive, and impart to the air electrical charges when they reach an obstacle. The solution of dissociable compounds usually diminishes this effect, whilst that of organic compounds markedly increases it. The formation of "double-layers" at the surface of separation is the cause usually assigned to these phenomena. The author has endeavoured to determine this difference of potential in the case of various liquids. The paper contains details of the method, the essential principle of which is the measurement of the E.M.F. of the chains $n\text{KCl} \mid \text{liquid 1} \mid \text{air} \mid \text{liquid 2} \mid n\text{KCl}$, and $n\text{KCl} \mid \text{liquid 1} \mid \text{liquid 2} \mid n\text{KCl}$. Experiments were made with solutions of hydrochloric, nitric, and sulphuric acids, and sodium sulphate; formic, acetic, and butyric acids, ethylic and amylalcohols; ether and ethylic benzoate. As expected, the effect of the electrolytes was small, but that of the non-electrolytes was frequently very considerable, whilst in most cases the velocity of formation of the double layer is so great as to be independent of the velocity of formation of the liquid surface. The absolute potential differences were calculated on the assumption that between air and a 0.011 per cent. solution of sodium chloride, no difference of potential exists, Lenard having found that when drops of this solution fall upon an obstacle no electric charges are produced. Curves are given with E.M.F. ordinates and concentration abscissæ, the character of the curves being very similar to those in which the ordinates represent the lowering of the surface tension of water. Experiments were also made in which illuminating gas replaced air, but this substitution appeared to have little, if any, effect on the potential differences. L. M. J.

Catalytic Action of Nitrous acid and the Potential of Nitric acid. By RUDOLF IHLE (*Zeit. physikal. Chem.*, 1896, **19**, 577—591).—If the oxidation of the hydrogen ions in the case of a Grove's cell is not sufficiently rapid, polarisation occurs, and the E.M.F. falls considerably. This oxidation velocity is largely dependent on the concentration of the acid, and is increased by the addition of small quantities of nitrous acid. Thus, although polarisation with a pure acid occurred when the concentration was 35 per cent., by the addition of 5 drops of a nitrite solution the acid could be further diluted to 20 per cent. without any polarisation. Owing to this action of nitrous acid, urea and strong oxidising agents, such as potassium permanganate, have a retarding effect on the oxidation velocity, which may further be increased by some reducing agents. The potential of the nitric acid increases with the concentration, the values 1.23 volt at 6 per cent., and 1.52 volt at 95.5 per cent. being obtained. Nitrous acid, however, lowers the potential, and its effect in this respect was found to be a logarithmic function of its concentration. The potential of nitrous acid itself was found to be lower than that of nitric acid. L. M. J.

Polarisation and Resistance of a Galvanic Cell. By FRANZ STREINTZ (*Ann. Phys. Chem.*, 1896, [2], **57**, 711—730).—In any closed

circuit containing a galvanic cell and a voltameter, it is impossible to obtain any method for determining the polarisation during the course of electrolysis. For, as the author shows, not only is the electromotive force a function of the strength of the current, but the resistance also changes with this, or rather with the density of the current on the electrodes.

H. C.

Measurement of the Electrochemical Forces of Accumulators. By PAUL SCHOOP (*Chem. Centr.*, 1895, i, 521; from *Zeit. Electrotechn. u. Electrochemie*, 1894, 234—243).—Attention is called to the present method of estimating the efficiency of accumulators only from the ratio of the charge given to that obtained from the cell, and it is pointed out that this does not afford a criterion of the suitability of the different types of accumulator for special purposes. The durability is never determined, but merely deduced from practical experience. In measurements of the efficiency and durability, attention should be simultaneously directed to the seven principal parts of any secondary cell, the active material of the positive and that of the negative plate, the materials of the plates themselves, the electrolyte, the insulation between the electrodes, the containing vessel. The author gives an account of experiments on accumulators in which these different points are taken into consideration, and shows that they afford data for estimating the suitability of secondary cells for different purposes. An improved form of cell is described, in which, by means of a special arrangement of the plates, a continual circulation of the electrolyte is rendered possible.

H. C.

Electromotive Force and Partition Equilibrium. By ROBERT LUTHER (*Zeit. physikal. Chem.*, 1896, 19, 529—571).—The author deduces theoretically the conclusion that electric cells consisting of different solutions in equilibrium with the same solution (for example, saturated solutions in different solvents) should possess an E.M.F. independent of the nature of the second solvent. This is proved in the case of the chains $\text{Hg} \mid \text{HgSO}_4 \mid \text{saturated ZnSO}_4 \mid \text{Zn}$, $\text{Hg} \mid \text{HgSO}_4 \mid \text{saturated CdSO}_4 \mid \text{Cd}$, and $\text{Hg} \mid \text{HgSO}_4 \mid \text{saturated CuSO}_4 \mid \text{Cu}$, the solvents being methylic and ethylic alcohols at different concentration. For the zinc chain, the E.M.F. was found to be 1.423, the other metals yielding the values 1.057 and 0.358, and the result was practically independent of the temperature. By a similar series of experiments with N/10 and N/100 solutions, curves were obtained for E.M.F./alcoholic content, from which, by the close coincidence of the methylic and ethylic alcohol curves, it appears that solutions in these solvents of equal concentration are approximately in equilibrium. From the curves may also be found the alcoholic content of a saturated solution required to be in equilibrium with a definite aqueous solution. The difference of potential for $\text{Hg} \mid \text{HgSO}_4$ in aqueous alcohol was determined by the aid of a capillary electrometer at different alcoholic (methylic and ethylic) content, and hence the author obtains the values for $\text{Zn} \mid \text{ZnSO}_4$, $\text{Cd} \mid \text{CdSO}_4$, and $\text{Cu} \mid \text{CuSO}_4$. The + potential difference falls rapidly with increasing alcoholic concentration, hence indicating that the dissociation decreases more rapidly than the solution tension of the metal. The differences of potential be-

tween the aqueous and alcoholic solutions (N/10 and N/100) are also calculated, the values being independent of the concentration and of the nature of the kation. This potential difference, as well as the alteration of the potential difference, metal | electrolyte, is greater for the solvent possessing the smaller dielectric constant, namely, ethylic alcohol.

L. M. J.

Use for Laboratory Purposes of the Electric Arc from the Low Potential Alternating Current. By MILO S. WALKER (*Amer. Chem. J.*, 1896, **18**, 323—328).—The author suggests, for high temperature experiments, the use of an electric arc obtained from an alternating current of low potential (about 50 volts and 1—5 ampères), the current being regulated by means of a rheostat capable of transmitting 12 ampères. Such an arc may be used for the following purposes: (1) To show the effect of high temperatures on substances which are "non-volatile" or fusible only with difficulty. (2) For reducing metallic oxides. (3) As a partial substitute for the blowpipe in qualitative analysis. (4) For the synthetic production of some carbon compounds from their elements.

The compound experimented on is conveniently retained in a conical cavity in the lower carbon, and the author further suggests that, where the object of the experiment is the reduction of oxides, a tube of carbon be used in place of the common rod-form of the upper carbon; in such a case, a stream of hydrogen or coal-gas, passed through the central core while the metal is cooling, will effectually prevent reoxidation.

A. L.

Conductivity of Yttrium Sulphate. By HARRY C. JONES and CHARLES R. ALLEN (*Amer. Chem. J.*, 1896, **18**, 321—323).—The molecular conductivity of yttrium sulphate in solutions of varying degrees of concentration was determined with the aid of the Kohlrausch apparatus. The results are given in the following table, where ν = number of litres of solution containing a $\frac{1}{2}$ gram-molecule of the sulphate, and $\mu\nu$ = corresponding molecular conductivity.

ν .	$\mu\nu$.	ν .	$\mu\nu$.
6.49	23.2	1161.44	102.6
12.98	27.8	3322.88	123.8
25.96	32.5	6645.76	152.6
51.92	38.5	13291.52	192.9
103.84	36.9*	26583.00	240.7
207.68	54.0	53166.00	333.8
415.36	66.6	106332.00	601.1
830.72	78.8		

A. L.

Conductivity of Solutions of Acetylene in Water. By HARRY C. JONES and CHARLES R. ALLEN (*Amer. Chem. J.*, 1896, **18**, 375—377).—The acetylene was prepared by heating cuprous acetylide

* This is probably a misprint for 46.9 (Abstractor).

with a solution of potassium cyanide. The strength of the solution was ascertained within two or three minutes of the measurement of conductivity at 0° by drawing off a known volume in a pipette, adding a N/10 solution of silver nitrate and an exactly equivalent quantity of potassium chloride, and then titrating the excess of potassium chloride by means of silver nitrate, potassium chromate being used as an indicator.

In the table, v = volumes in litres, which contains $\frac{1}{2}$ gram-molecule of acetylene, μ_v = molecular conductivities at the volumes v .

v .	μ_v .
417	29.0
833	41.0
1111	50.0
2502	77.0

Although somewhat vitiated by unavoidable errors due to loss of gas from the solutions, these numbers show that solutions of acetylene in water are somewhat dissociated, and that this dissociation increases with the degree of dilution. These results are in accord with the feebly acid character of the compound. A. G. B.

Decrease of Conductivity when the Water of Solution is replaced by Alcohol. By J. F. CARL SCHALL (*Zeit. physikal. Chem.*, 1896, **19**, 699—700; see Abstr., 1894, ii, 439).—A note regarding the purity of the methylic and ethylic alcohols employed in the observations recorded in the former paper. The author notes the peculiarity that, after prolonged dehydration of methylic alcohol, renewed distillation over sodium produced an increase in the conductivity. L. M. J.

Heats of Electrolytic Dissociation of some Acids. By FREDERICK L. KORTRIGHT (*Amer. Chem. J.*, 1896, **18**, 365—371).—The author has determined the heats of electrolytic dissociation of a number of acids of different but allied constitution. The measurements were made by the Ostwald-Kohlrausch method (Ostwald, *Handb. physiko-chemische Messungen*, 266). The actual measurements and the formulæ, by means of which the value of the heats of electrolytic dissociation were calculated from them, are given. In the following table, positive q is the heat absorbed if the electrolytic dissociation takes place without outside work.

Acid.	q 12.5° .	Acid.	q 12.5° .
Acetic	—428 cal.*	Phthalic.....	+162 cal.
Chloracetic....	—999 „	Isophthalic....	+2260 „
Bromacetic....	—790 „	Succinic.....	+1697 „
Dichloracetic..	—2924 „ †	Maleic.....	+846 „
Malonic	+966 „	Fumaric.....	+970 „
Butyric	—696 „	Mesaconic.....	+518 „
Benzoic	—335 „	Citraconic.....	—522 „

* From Jahn's table at 18° .

† „ Arrhenius's table at 21.5° .

These figures confirm the result of Arrhenius and Jahn that mono-basic acids dissociate electrolytically with development of heat, and show that the latter is increased by the introduction of a halogen atom, the effect of a second halogen atom being greater than that of the first. On the other hand, the introduction of a carboxyl group into the acid causes an absorption of heat, and the further the carboxyl groups are removed from each other the greater the absorption.

A. G. B.

Formation of Ammonia by the Electrolysis of Nitric acid.

By RUDOLF IHLE (*Zeit. physikal. Chem.*, 1896, **19**, 572—576).—The author investigated the conditions under which ammonia is formed at the cathode during the electrolysis of nitric acid, the formation being found to depend on both the current density and the strength of the acid. Thus for acids of 14.67, 28.73, 43.34, and 85.37 per cent. HNO_3 , current densities of 0.00159, 0.01122, 0.0564, and 8.6 ampères/sq. cm. were respectively required before any trace of ammonia was obtained. With increased currents, the quantity of ammonia formed was also increased.

L. M. J.

Absorption of Radiant Heat by Liquids.

By RICHARD ZSIGMONDY (*Ann. Phys. Chem.*, 1896, [2], **57**, 639—645).—Basing his observations on the experiments of Friedel (*Ann. Phys. Chem.*, 1895, [2], **55**, 453), the author points out that certain radicles or groups of elements exercise a very marked influence on the absorption of radiant heat by liquids. This is particularly noticeable in the case of the hydroxyl and amidogen groups, the introduction of which into any liquid hydrocarbon serves to greatly increase the absorption of radiant heat by these liquids. The author compares the behaviour of these groups with that of the auxochromic groups which convert coloured or colourless substances into dye-stuffs. It appears, further, that it is these auxochromic groups, to which amidogen and hydroxyl belong, which increase the absorption of radiant heat by colourless liquid hydrocarbons, and therefore that such groups increase generally the absorptive power of substances into which they are introduced.

H. C.

Boiling Points in a Cathode-light Vacuum.

By FRIEDRICH KRAFFT and H. WEILANDT (*Ber.*, 1896, **29**, 1316—1328).—A mercury manometer affords no accurate measurement of very low pressures. Using von Babo's pump (this vol., ii, 89), the pressure can be reduced to about a millionth of an atmosphere, as is indicated by the appearance of the green fluorescence in the glass of a Hittorf's tube attached to the distillation apparatus, when an induction current is sent between the platinum terminals. The distillation flask used had a capacity of about 15 c.c., and was in one piece with the receiver; the tube leading to the pump and to the Hittorf's tube was connected with the end of the receiver by means of an india rubber stopper or a ground glass joint, and the thermometer passed through a rubber stopper in the neck of the flask. The receiver was covered with moist filter-paper on which lumps of ice were placed; it was, of course, only possible to experiment with substances that, at this temperature of the receiver, have no appreciable vapour pressure;

with more volatile substances, a vacuum of a millionth of an atmosphere cannot be obtained. Such substances are the higher paraffins; cetylic alcohol, chloride, and iodide; the higher fatty acids and their amides; the higher acids of the oleic and oxalic series; alkylbenzenes of high molecular weight; mixed aliphatic-aromatic ketones of high molecular weight; and lastly, sulphobenzide and dinaphthyl sulphides and sulphone. It was found that in all these cases a great lowering of boiling point was brought about by the last small reduction of pressure; the difference in the boiling point under 15 mm. pressure and in the cathode-light vacuum varied, for the substances examined, from 70° to 100°.

C. F. B.

Thermochemistry of Oxybromides and Oxychlorides of the Calcium Group. By TASSILLY (*Compt. rend.*, 1896, **122**, 812—814).—The author has measured the heat of dissolution in dilute hydrobromic acid of the oxybromides of the metals of the calcium group (*Abstr.*, 1895, ii, 45 and 304), and from the results has deduced the heat of formation of the solid salts from their proximate constituents.

	Heat of dissolution.	Heat of formation.	
		Liquid water.	Solid water.
(1) $\text{CaBr}_2, 3\text{CaO}, 3\text{H}_2\text{O} \dots$	+95.7 Cal.	+66.7 Cal.	+62.5 Cal.
(2) $\text{SrBr}_2, \text{SrO}, 9\text{H}_2\text{O} \dots$	+16.45 "	+54.35 "	+41.75 "
(3) $\text{SrBr}_2, \text{SrO}, 3\text{H}_2\text{O} \dots$	+38.30 "	+32.5 "	+28.3 "
(4) $\text{BaCl}_2, \text{BaO}, 5\text{H}_2\text{O} \dots$	+18.5 "	+39.2 "	+32.2 "
(5) $\text{BaBr}_2, \text{BaO}, 5\text{H}_2\text{O} \dots$	+19.5 "	+41.2 "	+34.2 "
(6) $\text{BaBr}_2, \text{BaO}, 2\text{H}_2\text{O} \dots$	+33.80 "	+26.90 "	+24.1 "

The barium oxychloride was dissolved in dilute hydrochloric acid. The lower hydrates are obtained by carefully heating those which contain a larger proportion of water.

C. H. B.

Heat of Combustion of Cyanogen Derivatives. By J. GUINCHANT (*Compt. rend.*, 1896, **122**, 943—945).—

	Heat of combustion, 1 gram.	Molecular heat of combustion.		Heat of formation.
		Const. vol.	Const. pres.	
Cyanacetic acid...	7047	299.4	299.0	87.2
Cyanacetamide...	4485	376.7	376.4	44.2
Cyanacetophenone.	7487	1085.7	1086.1	3.6
Benzoic cyanide ..	7180	940.6	940.7	-14.2

Comparison of these results and also of those of other observers, for a large number of cyanogen derivatives, with those obtained with the compounds from which they have been derived, the necessary corrections for differences of physical condition being made, shows that the substitution of cyanogen for hydrogen in the group CH_3 or CH_2 in union with other carbon radicles increases the heat of combustion by about 90 Cal., or reduces the heat of formation by about 30 Cal. No relation can be traced between the differences between the heats of combustion and the intensity of the acid function of the cyanogen derivative.

C. H. B.

Heats of Solution and Neutralisation of Nitrocarbamide.

By SIMEON M. TANATAR (*Zeit. physikal. Chem.*, 1896, **19**, 696—698).—The heat of solution is -6.175 Cal.; of neutralisation $+9.277$ (18°); $+9.075$ (9°); and the heat of solution of the potassium salt is obtained as 10.195 . With excess of alkali, the value 9.478 Cal. was obtained on neutralisation, owing probably to a decrease in the dissociation. The heat of decomposition of the potassium salt by hydrogen chloride was $+4.480$, the difference in the heats of neutralisation being $+4.463$. With excess of acid, however, the value $+5.291$ was obtained, so that nitrocarbamide has still slightly basic properties.

L. M. J.

Thermochemistry of Hippuric acid, of its Homologues, and of Anisuric acid. By FRIEDRICH C. A. STOHMANN and RAYMUND SCHMIDT (*J. pr. Chem.*, 1896, [2], **53**, 345—369).—It has been previously shown (Abstr., 1894, ii, 340) that the substitution of CH_2COOH , for H in an amido-group increases the heat of combustion by 162.7 cal. From this datum and the known heat of combustion of benzamide, the heat of combustion of hippuric acid may be calculated to be 1010.5 cal.; one of the authors previously found it to be 1014.5 , and Berthelot and André give 1012.9 . The re-determined value is 1012.6 . The following table comprises the results of the present investigation. The calculated values are deduced as indicated above. In those cases in which the heat of combustion of the amide is not known, it is deduced from that of the parent acid, for this value has been shown to be smaller than the heat of combustion of the amide by 75.9 cal.

	Heat of combustion at constant pressure.		Heat of formation, cal.	100 k.
	Found, cal.	Calculated, cal.		
Hippuric acid, $\text{C}_9\text{H}_9\text{NO}_3$	1012.6	1010.5	143.9	0.0222
Orthotoluric acid, $\text{C}_{10}\text{H}_{11}\text{NO}_3$	1168.2	1168.0	151.3	0.0192
Metatoluric „ $\text{C}_{10}\text{H}_{11}\text{NO}_3$	1167.6	1167.7	151.9	0.0208
Paratoluric „ $\text{C}_{10}\text{H}_{11}\text{NO}_3$	1168.1	1166.0	151.4	0.0199
Benzoylalanine, $\text{C}_{10}\text{H}_{11}\text{NO}_3$	1168.7	1167.1	150.8	0.0194
Benzoylsarcosine, $\text{C}_{10}\text{H}_{11}\text{NO}_3$	1180.9	1177.1	138.6	0.0499
Phenaceturic acid, $\text{C}_{10}\text{H}_{11}\text{NO}_3$	1165.5	1166.2	154.0	0.0203
Orthotoluoylalanine, $\text{C}_{11}\text{H}_{13}\text{NO}_3$	1322.3	1324.6	160.2	0.0165
Paratoluoylalanine, $\text{C}_{11}\text{H}_{13}\text{NO}_3$	1320.0	1322.6	162.5	0.0168
Anisuric acid, $\text{C}_{10}\text{H}_{11}\text{NO}_4$	1135.7	1133.8	183.8	0.0161

That the three toluric acids should have virtually identical heats of combustion is contrary to expectation, seeing that an ortho-derivative nearly always has a higher heat of combustion than the corresponding meta-compound has, and that the meta-compound generally shows a higher value than the para-compound. Ortho- and paratoluoylalanine are normal in this respect. It will be noticed that the heats of combustion of corresponding homologues in the above list differ

by from 151.9 to 155.6 cal., showing that the approximately regular increase of 156.6 cal. for the addition of CH_2 obtaining in the fatty series (Abstr., 1894, i, 224) is not maintained in the aromatic series.

The entry of a benzoyl group in place of a hydrogen atom in the amido-group raises the heat of combustion by a mean value of 779.6 cal.; similar substitution of a toluoyl group produces a rise of 933.4 cal.

The heat of combustion of phenylacetic acid has been found to be 933.2 cal. This value is not in accord with those found for benzoic acid and phenylpropionic acid, namely 771.7 cal. and 1085.5 cal. respectively; it will be seen that the difference between benzoic acid and phenylacetic acid is 160.5 cal., that between phenylacetic acid and phenylpropionic acids being only 152.2 cal. All analogies indicate that these differences should be more nearly equal than they appear to be. A re-determination, made on a carefully purified specimen of phenylacetic acid, gave 930.7 cal., but this number is believed to be too high, more especially as the value calculated from the heat of combustion of phenaceturic acid is 926.9 cal., and because the conductivity of phenylacetic acid shows it to be a more feeble acid than any of the toluic acids whose heats of combustion range from 929.4 cal. to 927.4 cal. Now the feeblest acid is not likely to have the highest heat of combustion, hence the authors conclude that they have not yet obtained a pure specimen of phenylacetic acid. They adopt the provisional value of 927.6 cal. for the constant in question. A. G. B.

Use of Phenolphthaleïn in illustrating the Dissociating Action of Water. By HARRY C. JONES and CHARLES R. ALLEN (*Amer. Chem. J.*, 1896, 18, 377—381).—The authors seek to explain the fact that ammonia will not develop a red colour in an alcoholic solution of phenolphthaleïn until a certain proportion of water has been added, whilst potassium hydroxide will immediately develop a red colour in the alcoholic solution (compare Menshutkin, Abstr., 1883, 550), by reference to the theory of ionic dissociation. They give details of measurements to show that the molecular conductivity of a solution of potassium hydroxide in a mixture of alcohol and water is higher than one of ammonia of corresponding concentration.

A. G. B.

Behaviour of Soap-like Substances in presence of Water. V. By FRIEDRICH KRAFFT and A. STRUTZ (*Ber.*, 1896, 29, 1328—1334).—It has been shown (this vol., i, 80) that the sodium salts of the lower fatty acids raise the boiling point of water by twice the normal value; this was explained by supposing each molecule to be "hydrolytically decomposed" into sodium hydroxide and fatty acid. It was also shown that the sodium salts of the higher fatty acids, when dissolved in water so as to form strong (15—20 per cent.) solutions, do not raise the boiling point of the water at all, whilst the solutions solidify on cooling to gelatinous masses; this behaviour is characteristic of colloid substances. It is now shown that sodium oleate in alcoholic solution does not exhibit this behaviour; it raises the boiling point by about half the normal amount, which may be explained by the existence of double molecules.

Hexadecylamine hydrochloride was next examined, because in a

certain sense it is the antipode of such a substance as sodium oleate; if water decomposes it, it will be into an inorganic acid (hydrochloric) and an organic base (hexadecylamine) of high molecular weight, whereas sodium oleate is decomposed into an inorganic base (sodium hydroxide) and an organic acid (oleic) of high molecular weight. As a matter of fact, it was found to exhibit, in aqueous solution, the behaviour of a colloïd substance; in alcoholic solution, it caused a normal rise in the boiling point. Further, just as the lower "soaps,"—sodium acetate, for example—behaved like crystalloids in alcoholic solution, and, owing to their "hydrolytic decomposition," gave only half the normal rise of boiling point, so the lower amine hydrochlorides,—methylamine hydrochloride, and also ammonium chloride itself,—were found to exhibit precisely the same behaviour; it is assumed that they were decomposed into hydrochloric acid and amine (ammonia).

Lastly, hexadecylamine palmitate, a compound of an organic amine with an organic acid, both of high molecular weight, was examined. Even in dilute solution ($2\frac{1}{2}$ per cent.) it exhibited the behaviour of a colloid substance.

It will be noticed that the term "hydrolytic decomposition" is not used in the same sense as by the adherents of the electrolytic dissociation theory. It may also be remarked that there is no discussion in the paper of the possibility that it is by virtue of their dissociation into ions that sodium acetate, methylamine hydrochloride, &c., raise the boiling point of water by twice the normal amount. C. F. B.

A Theory of Colloïdal Solutions. By FRIEDRICH KRAFFT (*Ber.*, 1896, 29, 1334—1344; compare this vol., i, 80, and preceding abstract).—The following two laws are enunciated.

I. *Colloïdal Liquids or Solutions contain the Liquefied Substance in the Molecular State.*—By "molecular state" is meant, presumably, in the state of single molecules, and not in that of molecular aggregates. The sodium salts of the lower fatty acids exist in the "molecular state" in aqueous solution; and they give twice the normal rise of boiling point, which corresponds with a "hydrolytic decomposition" into sodium hydroxide and the fatty acid. Now the sodium salts of the higher fatty acids, which have been shown to behave as colloïds, yield dilute aqueous solutions which begin to crystallise at temperatures only slightly below the solidifying points of the corresponding acids themselves. And a strong (15—20 per cent.) aqueous solution of sodium stearate has even been found to solidify (to a gelatinous mass) at the same temperature as that at which stearic acid itself solidifies or melts. (The free salts, it may be said, do not melt or decompose until about 250° .) It would seem thus that the sodium salts of the higher fatty acids, like those of the lower, are decomposed in aqueous solution, colloïds though they be, into sodium hydroxide and fatty acid. Now palmitic acid, dissolved in ether, lowers the boiling point by the normal amount, and therefore must exist as single molecules at temperatures as low as that of boiling ether. From these facts the conclusion is drawn that "colloïdal soap solutions contain the dissolved soaps in the molecular state."

II. *Colloïdally Liquefied Molecules rotate in very small Closed Orbits or Surfaces.*—The molecules of crystalloïds in solution are regarded as having a motion similar to that of gaseous molecules; their motion of translation gives rise to osmotic pressure and the accompanying phenomena of lowering of freezing point and raising of boiling point. Now it has been shown that the distinction between colloid and crystalloid substances does not consist in a difference of molecular aggregation. This distinction manifests itself in an absence of influence on the boiling point of the solvent, from which we may infer an absence of appreciable motion of translation; the motion of the molecules of dissolved colloïd substances is, therefore, one of rotation. It is further suggested that the structural unit, so to speak, of a colloïdal solution is a "proto-cellular bubble" of extremely small dimensions, the surface of the bubble being formed by molecules of the dissolved colloïd, whilst the interior is filled with the solvent. In this connection, it is interesting to note that bubbles of a solution of a colloïd substance can be blown, and can exist, only at temperatures approaching, to or above, that at which the colloïd solution begins to be formed; that is, above the temperature at which the colloïd solution gelatinises when it is cooled. In this respect, hexadecylamine hydrochloride behaves like sodium stearate. If we assume that "proto-cellular bubbles" are also the structural units of organised substances, it is thus easy to understand why a certain minimum temperature is essential to the life of organised beings.

C. F. B.

Solid Solutions formed by Non-isomorphous Substances.

By FELICE GARELLI (*Gazzetta*, 1896, 26, i, 61—88).—The author has previously shown (Abstr., 1894, i, 157) that many substances give anomalous results by the cryoscopic method, owing to a tendency which they have to form solid solutions with the solvent employed; this is due, in most cases, to isomorphism between the dissolved substance and the solvent. It is now shown from crystallographic data compiled by Negri that isomorphism will not account for all cases of anomalous depression of the freezing point. Benzoic acid is not isomorphous with its hydroxy- or amido-derivatives, and the crystallographic relationship between benzoic acid on the one hand, and para- and ortho-hydroxybenzoic acids on the other, are almost the same; paramidobenzoic acid is crystallographically much more like benzoic acid than is its ortho-isomeride, although the behaviour of para-derivatives in benzoic acid solution is more nearly normal than that of the ortho-compounds. Similarly there is a close crystallographic analogy between benzoic acid and the pyromucic and pyrrolinocarboxylic acids, although only the latter behaves abnormally in freezing benzoic acid. On the other hand, succinic and maleïc anhydrides are isomorphous, as would be expected from their cryoscopic behaviour.

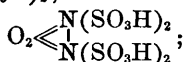
The author has further investigated the formation of solid solutions by Bijlert's method, which consists in adding to the solution a third substance which cryoscopically behaves normally; then on analysing the solid separating on cooling the solution, the proportion of the third substance present tells the amount of mother liquor

carried down mechanically. The formation of solid solutions of salicylic acid in benzoic acid was thus demonstrated, using diphenylamine or anthracene as the third substance. W. J. P.

"Indirect" Etherification. By JULIUS TAFEL (*Zeit. physikal. Chem.*, 1896, 19, 592—598).—The author considers that Peterssen's indirect etherification (Abstr., 1895, ii, 258) is due, not to the action of the methylic chloride, but to the catalytic action of hydrogen chloride. His experiments show that the accelerative influence of pure methylic chloride is very small compared with that of the acid. Thus the ratios k/k_0 of the velocity constants in the presence and absence (1) of methylic chloride, and (2) of hydrogen chloride of equal chlorine content, are respectively 3 and 1410. The ratio k/k_0 is, however, not proportional to the quantity of acid. L. M. J.

The Catalytic Action of Hydrogen Ions in Polymolecular Reactions. By ARTHUR A. NOYES (*Zeit. physikal. Chem.*, 1896, 19, 599—606).—According to Magnanini's observations, the accelerative effect of acids on the velocity of the reaction between bromic and hydriodic acids increases more rapidly than the concentration of the added acid (Abstr., 1892, 110). The reaction was shown by the author to be of the second order (this vol., ii, 158), and from Magnanini's numbers he proves that the velocity is proportional to the square of the concentration of the acid. In the case of the reaction between hydrogen peroxide and hydrogen iodide, the increase of the velocity is proportional to the added acid. From this, it appears as if the acceleration were due to an increased activity of the reacting compounds; in the latter case, the activity of one of the compounds only being increased. In the case of the reaction between ferric chloride and stannous chloride, a reaction of the third order (Abstr., 1895, ii, 257), the acceleration, as deduced from Kahlenberg's experiments (Abstr., 1894, ii, 346), appears also to be proportional to the square of the concentration. L. M. J.

Decomposition Velocity of Acids containing both Sulphur and Nitrogen. By MAX WAGNER (*Zeit. physikal. Chem.*, 1896, 19, 668—688).—The decomposition velocity was studied in the cases of a number of acids which may be regarded as derived from ammonia by the displacement of the hydrogen by hydroxyl and sulphonic acid groups. The decomposition was usually effected by the action of dilute acids on the aqueous solution of the acid or its potassium salt. Measurements of the velocity were obtained in the cases of imidosulphonic acid, $\text{NH}(\text{SO}_3\text{H})_2$; nitrogen trisulphonic acid, $\text{N}(\text{SO}_3\text{H})_3$; nitrosohydroxylaminesulphonic acid, $\text{NO}\cdot\text{N}(\text{OH})\cdot\text{SO}_3\text{H}$; hydroxylaminedisulphonic acid, $\text{OH}\cdot\text{N}(\text{SO}_3\text{H})_2$; sulphazotic acid, $\text{O}_2[\text{NH}(\text{SO}_3\text{H})_2]_2$; oxy-sulphazotic acid, $2\text{NO}(\text{SO}_3\text{H})_2$; and nitrotrisulphonic acid,



whilst other acids were examined without, however, measurements of the velocity being obtainable. Determinations were also obtained with the phenyl-, tolyl- (ortho-, meta-, and para-); xylyl- (ortho-,

meta-, and para-); chlorophenyl- (ortho-, meta-, and para-); and β -naphthylsulphamic acids. The entrance of the hydrocarbon groups is found to increase the velocity of decomposition. In this respect the more complex groups exert a greater influence than the phenyl group, except in the case of the meta- and para-tolylsulphamic acids, whilst the velocity becomes practically zero for the nitro- and methyl-phenyl-compounds, and infinite for the β -naphthyl acid.

L. M. J.

Analytical Representation of the Periodic System of the Elements. By DMITRI A. GOLDHAMMER (*Zeit. anorg. Chem.*, 1896, **12**, 39—45).—If the chemical character of an element of atomic weight p is denoted by e , then $e = F(p)$ is the equation to a periodic curve. If further the value of e at certain points passes through $\pm\infty$, the curve will consist of a number of separate portions, each of which will represent a distinct period. These portions will be in no way identical, although similar in form.

Flavitzky and Thomsen have independently suggested the cotangent as fulfilling the required properties of the function; but the author regards it as more probable that the function is of a more complex order.

H. C.

Inorganic Chemistry.

Density of Hydrogen and Oxygen. By JULIUS THOMSEN (*Zeit. anorg. Chem.*, 1896, 12, 1—15; see also this vol., ii, 244).—The density is obtained by determining the volume of a known weight of the gas in a similar manner to that in which the ratio of the atomic weights was determined. A full description of the apparatus employed is given in the original paper. The volume of the weight of hydrogen evolved from the dissolution of a known weight of aluminium in a solution of potassium hydroxide was determined, and the volume of the weight of oxygen evolved by heating a mixture of 4 parts of fused potassium chlorate, 3 parts of compact ferric oxide, and 3 parts of porous ferric oxide.

The results obtained, calculated for latitude 45° at 0° and 760 mm., are as follows. Weight of 1 litre of hydrogen, 0.089947 gram; weight of 1 litre of oxygen, 1.42906 gram; ratio of the densities, 1 : 15.8878; ratio of the atomic weights, 1 : 15.8690; ratio of the volumes in the formation of water, 1 : 2.00237; volume of 1 gram of hydrogen, 11.1176 litres; volume of 1 gram of oxygen, 0.69976 litres.

E. C. R.

Decomposition of Silver Oxide by means of Hydrogen Peroxide. By E. RIEGLER (*Chem. Centr.*, 1895, ii, 545; from *Bull. Soc. Sci. Fiz.*, Bukarest, 4, 78—80).—At one time it was generally believed that the reaction between silver oxide and hydrogen peroxide was represented by the equation $\text{Ag}_2\text{O} + \text{H}_2\text{O}_2 = \text{Ag}_2 + \text{H}_2\text{O} + \text{O}_2$, until Berthelot substituted for this $2\text{H}_2\text{O}_2 + 4\text{Ag}_2\text{O} = 2\text{H}_2\text{O} + 2\text{Ag}_2 + 2\text{Ag}_2\text{O} + \text{O}_2$.

After carefully going into the matter, the author now states that neither of these equations is correct, but that they must be replaced by the following ones: $3\text{H}_2\text{O}_2 + 2\text{Ag}_2\text{O} = 3\text{H}_2\text{O} + \text{Ag}_4\text{O} + 2\text{O}_2$;
 $\text{Ag}_4\text{O} = \text{Ag}_2 + \text{Ag}_2\text{O}$.
 L. DE K.

New Electrolytic Method. By THEODOR GROSS (*Chem. Centr.*, 1895, i, 411—412; from *Electrochem. Zeits.*, 1894, 1, 80—84).—By the electrolysis of a solution containing 1 part of silver sulphate, 2—3 parts of silver oxide, and 120 parts of a 10 per cent. solution of ammonia, using mercury electrodes containing silver, the author obtains the separation at the anode of a grey mass, which is coloured white when heated with nitric acid, loses mercury when heated alone, and leaves a brownish-yellow, fusible residue. This residue appears to contain an entirely new substance, which the author regards as a decomposition product of the sulphur contained in the silver sulphate. After removal of the mercury and silver present, a dull grey powder is obtained which is insoluble in nitric acid, and dissolves in aqua regia to a yellow liquid, giving with hydrogen sulphide in the slightly acid solution a brown precipitate somewhat soluble in ammonium sulphide. This brown precipitate when heated, loses sulphur, and the original grey powder is recovered.
 H. C.

Action of Hydrogen Bromide and Hydrogen Iodide on Phosphorus Oxychloride. By ADOLPHE BESSON (*Compt. rend.*, 1896, 122, 814—817).—Dry hydrogen bromide has no action on phosphorus oxychloride at its boiling point, but if the gas is dissolved in the liquid and heated in sealed tubes at 200° , decomposition takes place. The best results are obtained by passing a mixture of gaseous hydrogen bromide and vapour of the oxychloride through a tube filled with pumice and heated at 400 — 500° . Under these conditions there is complete displacement of oxygen and chlorine by bromine, and the product contains phosphorus pentabromide. Other constituents of the product are POCl_2Br , POClBr_2 , and POBr_3 .

Phosphorus oxydichlorobromide, POCl_2Br , shows great tendency to remain in superfusion, but forms large, colourless lamellæ which melt at 13° ; it boils at 135 — 138° . The oxydibromochloride, POClBr_2 , shows a similar tendency; it melts at 30° and boils at 165° ; sp. gr. = 2.45 at 50° . When boiled in contact with air, the bromine is partially displaced by oxygen, and the product contains POCl_3 , POCl_2Br , and POBr_3 . In a sealed tube, the final products are POCl_3 and POBr_3 , the intermediate oxydichlorobromide, POCl_2Br , being decomposed by heat.

Hydrogen bromide acts energetically on phosphorus trichloride, but the product always splits up into the trichloride and the tribromide. If chlorobromides are formed, it would seem that they can only be separated by fractional solidification or melting.

Hydrogen iodide acts rapidly on phosphorus oxychloride at the ordinary temperature, with liberation of iodine, but at 0° the action is slower, and the product contains iodine, phosphorus triiodide, and metaphosphoric acid. There is some evidence that a crystallisable yellow phosphorus oxyiodide is also formed in small quantity, but it could not be definitely isolated.
 C. H. B.

Thiophosphates. By LUCIEN FERRAND (*Compt. rend.*, 1896, **122**, 886—889).—The author has prepared by Friedel's method a second series of thiophosphorus compounds which he terms *thiopyrophosphates*. Their general formula is $M'_4P_2S_7$ (compare *Abstr.*, 1895, ii, 389). The *cuprous* compound is a violet, crystalline compound, attacked by alkalis and acids with the exception of hydrochloric acid; no cupric compound could be obtained. The *ferrous* compound forms small, lustrous lamellæ, insoluble in cold nitric acid; the *silver* compound is a yellow, crystalline mass not attacked by boiling nitric acid, but decomposed by aqua regia; the *nickel* compound is a deep brown, crystalline powder, attacked by nitric acid at 150° ; the *chromous* compound crystallises in minute, black, hexagonal lamellæ; the *zinc* compound in small needles; the *cadmium* compound is white and crystalline, and but slightly attacked by acids; the *mercurous* compound is red and crystalline, and is not attacked by acids; the *lead* compound is red and crystalline, and is decomposed by hot nitric acid; the *aluminium* compound crystallises in small, white needles, and is very readily attacked by water, alkalis, and acids. The mercurous, zinc, cadmium, chromium, and nickel compounds are decomposed by water or moist air, although some of them offer considerable resistance to the action of acids. C. H. B.

Sulphoxyarsenates [Thioarsenates]. By R. F. WEINLAND and O. RUMPF (*Ber.*, 1896, **29**, 1008—1012).—By boiling aqueous sodium arsenite with the calculated quantity of precipitated sulphur, *sodium monothioarsenate*, $Na_3AsSO_3 \cdot 12H_2O$, can be obtained. The *potassium* salt can be prepared in the same way, but it is hygroscopic, and difficult to purify. To obtain the *ammonium* salt, $(NH_4)_3AsSO_3 \cdot 3H_2O$, the digestion has to be conducted under pressure; the salt rapidly loses ammonia when left exposed to the air.

Selenium behaves in a similar way, the compound,



being formed. Tellurium also adds itself on to some extent; the product obtained had a composition approximating to $Na_{12}As_4TeO_{15}$.

Monopotassium monothioarsenate, KH_2AsSO_3 , is best prepared by the action of salicylic acid on the tripotassium salt; by dissolving it in aqueous potassium hydroxide, the *dipotassium* salt can be obtained; this is very hygroscopic, and was not got pure.

Sodium dithioarsenate, $Na_3AsS_2O_2$, can be obtained in various ways, as by the addition of sodium bisulphide to sodium metarsenite, or by the action of sodium bisulphide on sodium orthoarsenite or monothioarsenate, other products being simultaneously formed. It has not been found possible, hitherto, to prepare a trithioarsenate, Na_3AsS_3O .

C. F. B.

Calcium Silicide. By GUILLAME DE CHAIMOT (*Amer. Chem. J.*, 1896, **18**, 319—321).—If silica, lime, and carbon, mixed in the proportions theoretically necessary for the production of calcium silicide, are fused in the electric furnace, calcium carbide is the main product, but is accompanied by silicide; when the silica is in excess, an impure calcium silicide is formed, but is contaminated with considerable

quantities of calcium carbide, silicon, and iron derived from the furnace. Specimens of the product vary considerably in appearance, but are all sufficiently hard to scratch glass, and show the reactions for calcium silicide described by Wöhler. They evolve hydrogen when placed in water, and in dilute hydrochloric acid form a yellow silicic acid; if in the latter instance the silicide be finely divided, hydrogen silicide is evolved. When boiled with hydrochloric acid, the silicide is decomposed, and crystals of silicon remain.

Calcium carbide, when fused with sand, forms a small quantity of calcium silicide. A. L.

Basic Magnesium Nitrate. By GASTON DIDIER (*Compt. rend.*, 1896, 122, 935—936).—Two hundred grams of hydrated, normal magnesium nitrate was dissolved in 150 c.c. of water, and to this solution, heated at 100°, was added in successive small quantities, 10 grams of magnesium oxide prepared by heating the basic carbonate at a temperature between 350° and 400° for several hours. Towards the end of the operation the liquid is heated to 150°, filtered through cloth, and allowed to remain for some time in closed vessels. After some days, a flocculent precipitate begins to form, and slowly increases and fills the whole vessel. When dried out of contact with carbonic anhydride, the product consists of slender, white, microscopic, optically active needles, of the composition $3\text{MgO}, \text{N}_2\text{O}_5, 5\text{H}_2\text{O}$. Water decomposes it completely into its proximate constituents and absolute alcohol has a similar effect. C. H. B.

Recent Work on Double Haloïds. By CHARLES H. HERTY (*Amer. Chem. J.*, 1896, 18, 290—294; compare Abstr., 1895, ii, 112).—Lenher (*J. Amer. Chem. Soc.*, 1895, 17, 511) has given no proof of the existence of the compounds $\text{PbI}_2, 2\text{KI}$ and $\text{PbI}_2, 4\text{KI}$, described by him as occurring in solution. The compound, $3\text{PbI}_2, 4\text{KI}$, described by Mosnier (Abstr., 1895, ii, 268) has repeatedly been shown to be incapable of existence, whilst those to which he assigned the formulæ $3\text{PbI}_2, 4\text{NH}_4\text{I}$ and $\text{PbI}_2, 2\text{NaI}$, are found on examination to be mixtures containing ammonium or sodium iodide.

The salt described by Miss Field (*Trans.*, 1893, 540) proves, on analysis, to have the composition $\text{NH}_4\text{I}, \text{PbI}_2 + 2\text{H}_2\text{O}$, and not $3\text{PbI}_2, 4\text{NH}_4\text{I}$, as stated by that author, and analyses of the compounds PbI_2Cl and $\text{PbI}_2, 3\text{PbCl}_2$ confirm the suggestion of Retgers (Abstr., 1895, ii, 309) that they are merely isomorphous mixtures.

A. L.

Relations between Copper and Concentrated Sulphuric acid. By CHARLES BASKERVILLE (*J. Amer. Chem. Soc.*, 1895, 17, 904—912).—The author has made a number of experiments showing the action of sulphuric acid on metallic copper at different temperatures, and tabulated the results.

The experiments were made in a current of carbonic anhydride so as to exclude the air. The insoluble black substance seems to be copper sulphide, but in one experiment an oxysulphide of the formula $\text{CuO}, 2\text{Cu}_2\text{S}$ was obtained. On the whole, the experiments, particularly those concerning the secondary reactions, confirm those of Pickering (*Trans.*, 1878, 112). L. DE K.

Rare Earths in Monazite Sands. By PAUL SCHÜTZENBERGER and O. BOUDOUARD (*Compt. rend.*, 1896, **122**, 697—699).—The metals in monazite sands which form sulphates soluble in a saturated solution of potassium sulphate, comprise metals of the yttrium group with a mean atomic weight of 105—106, and also a metal forming a colourless oxide, the equivalent of which is not altered by fractionation of either the nitrate or the sulphate; its atomic weight is very nearly 102 (101·95—102·4).
C. H. B.

New Element in Rare Earths of the Samarium Group. By EUGÈNE A. DEMARÇAY (*Compt. rend.*, 1896, **122**, 728—730).—Fractionation by crystallisation from concentrated nitric acid of earths very rich in samarium yielded a new nitrate more soluble in nitric acid than that of gadolinium but less soluble than that of samarium. The corresponding oxide differs from terbium in being colourless, and its salts are colourless, and show no absorption spectra. Its spark spectrum differs from those of lanthanum, cerium, gadolinium, ytterbium, and terbium. The new oxide, Σ_2O_3 , differs from lanthanum and cerium oxides by its relatively feeble basicity and the greater solubility of its double potassium sulphate; from ytterbium by its greater basicity and the lower solubility of its double sulphate. In both respects it resembles gadolinium and samarium, but gives a different spectrum.

The most characteristic lines in the spectrum of the new element Σ are 4228·1, 4205·9, 4128·4, 3972·2, 3930·8, 3819·9, whilst the most characteristic of gadolinium are 4263·1, 4178·2, 4098·6, 4063·4, 4049·9, 3959·9, 3958·1, 3916·7, 3852·6, 3850·9, 3549·3, 3545·7. None of either group can be attributed to terbium. Some samarium carefully purified by Clève was found to contain a very considerable proportion of the new element, and it seems probable that the true atomic weight of samarium is considerably below the value (150) now attributed to it.
C. H. B.

Reduction of Permanganic acid by Manganese Dioxide. By HARMON N. MORSE, A. J. HOPKINS, and M. S. WALKER (*Amer. Chem. J.*, 1896, **18**, 401—419).—The authors summarise their work as follows. (1) Permanganic acid and potassium permanganate are reduced by precipitated manganese dioxide with liberation of three-fifths of the active oxygen of the permanganic acid; (2) standard solutions of permanganate should be filtered through asbestos; (3) such filtered solutions exhibit a high degree of stability, whether kept in darkness or in diffused light; even pure solutions are, however, decomposed in direct sunlight; (4) the oxide produced by the complete reduction of a neutral solution of potassium permanganate contains all the potassium of the original salt, and the supernatant liquid is therefore neutral; (5) whether the precipitated manganese oxide is formed by the slow decomposition of a neutral solution of potassium permanganate or by the addition of manganese sulphate to an acidified solution of permanganic acid (*sic*), the ratio of oxygen to manganese in it remains normal (that is, 2:1) only so long as un-reduced permanganate or permanganic acid is present, otherwise the

oxide loses oxygen even at the ordinary temperature. In the presence of permanganate, the lost oxygen is restored. A. G. B.

Crystallised Iron Sesquiphosphide. By A. GRANGER (*Compt. rend.*, 1896, **122**, 936—937).—Iron sesquiphosphide, Fe_2P_3 , is obtained as a pale grey mass of hard, lustrous, non-magnetic, microscopic crystals by heating ferric chloride to dull redness in phosphorus vapour. The two substances are placed in separate dishes in the same tube, and the phosphorus vapour is carried over the iron salt by means of a current of carbonic anhydride.

The sesquiphosphide is insoluble in hydrochloric and nitric acids and in aqua regia; does not alter when heated in air to dull redness, but loses phosphorus at a bright red heat; and is slowly attacked by chlorine at dull redness, and by bromine at a higher temperature.

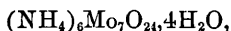
C. H. B.

Molybdenum Amalgam and some Properties of Molybdenum. By JULES FÉRÉE (*Compt. rend.*, 1896, **122**, 733—735).—Hydrochloric acid of 22° B. saturated with molybdic acid is diluted with nine times its volume of water, and electrolysed with a mercury cathode and a platinum anode, the current being about 5 ampères for each sq. cm. of mercury surface. After some time, the mercury is dried and filtered through chamois leather, when it yields a solid amalgam, MoHg_3 , which is but slightly affected by moist air. When it is subjected to a pressure of 200 kilos. per sq. cm., it yields another amalgam, MoHg_2 , and if this is broken up and again compressed, it yields a third compound, Mo_2Hg_3 , which alters rapidly in moist air. The decomposition of the amalgams under pressure is the inverse of the phenomena observed by Spring.

The molybdenum obtained from the amalgam by distillation in a vacuum at a low temperature is pyrophoric, but loses this property if heated above 400°. It absorbs sulphurous anhydride completely, becoming incandescent, and yielding a mixture of molybdenum sulphide and oxides. Nitrogen, carbonic anhydride, and hydrogen sulphide are without action, even when gently heated. Carbonic oxide is, however, rapidly decomposed with liberation of carbon and formation of molybdenum oxides. Nitric oxide is completely absorbed with incandescence, a mixture of molybdenum oxides and a nitride being formed.

C. H. B.

A new Perthiomolybdic acid. By KARL A. HOFMANN (*Zeit. anorg. Chem.*, 1896, **12**, 55—62).—The ammonium salt, $\text{MoS}_6\text{NH}_4\cdot\text{H}_2\text{O}$, is obtained as follows. A solution of ammonium molybdate,



(20 grams) in water (260 c.c.) is mixed with 7 per cent. ammonia (20 c.c.) and treated for four hours with hydrogen sulphide, whereby a solution of ammonium thiomolybdate, $(\text{NH}_4)_2\text{MoS}_4$, is obtained. This solution is mixed with a solution of ammonium polysulphide and allowed to remain 24 hours, when the salt separates in lustrous, black needles; a further quantity of the salt is obtained by carefully precipitating the mother liquors with alcohol. It is purified by washing with

water, then with alcohol, ether, and carbon bisulphide, finally drying over potassium hydroxide. It dissolves sparingly in water and alcohol with a yellowish-brown coloration. The *potassium salt*, MoS_6K , obtained by treating the ammonium salt with 10 per cent. potassium hydroxide for 24 hours at the ordinary temperature, crystallises in thin, dark brown leaflets, and is more soluble in water than the ammonium salt. The *caesium salt* crystallises in long, black needles, and is insoluble in water, the *thallium salt* in lustrous, black prisms, insoluble in water. The *free acid*, MoS_6H , is obtained by treating the ammonium salt with cold 10 per cent. hydrochloric acid, and then washing the product with carbon bisulphide.

When the above ammonium salt is warmed with a solution of potassium hydrosulphide in a current of hydrogen, it is converted into the pentathiomolybdate described by Krüss.

E. C. R.

Physical Properties of Phosphododecatungstic acid. By M. SOBOLEFF (*Zeit. anorg. Chem.*, 1896, **12**, 16—38).—*Phosphododecatungstic acid*, $\text{H}_3\text{PO}_4 \cdot 12\text{WO}_3 \cdot 21\text{H}_2\text{O}$, sp. gr. 4.68. Both the acid and its salts are easily soluble in water, and the solution shows the reactions of phosphoric and metatungstic acids, and gives precipitates with alkaloïds and peptones. The free acid is also soluble in ether and alcohol. When ether is added to an aqueous solution of the acid, heat is developed and three layers are formed, the top one is a layer of ether, the middle one a solution of the acid in water, and the bottom one a solution of the acid in ether. The acid, when partially dehydrated, can only be dissolved in ether when water, corresponding with the amount of dehydration, is added. There are two hydrates of the crystallised acid. The supersaturated solution, when quickly cooled, gives skeleton crystals belonging to the regular system, and then well-formed cubes and octahedra; the last form is the most stable, and is always obtained on cooling saturated solutions or by prolonged crystallisation in a desiccator. When these octahedra are separated from the solution they quickly become covered with six-sided stars, arranged parallel to the edges of the octahedron, and the crystals break up into new crystals which contain less water. The crystals of the second hydrate are obtained by crystallising a supersaturated solution in a thermostat at 50° . It crystallises in the rhombic system, $a : b : c = 0.94207 : 1 : 1.96187$. When the solution is quickly evaporated, long, thin needles are obtained, which act on polarised light. The *barium salt* crystallises in regular octahedra; the *sodium salt* in regular octahedra, sp. gr. 4.73; these are very unstable and give up their water of crystallisation on exposure to the air. Concentrated solutions, when crystallised in a thermostat at 80° , give crystals of a second hydrate, which crystallises in the triclinic system, $a : b : c = 1.08752 : 1 : 2.08137$. $\alpha = 85^\circ 21' 0''$, $\beta = 95^\circ 27' 54''$, $\gamma = 87^\circ 41' 30''$. The above crystallographic data and the conversion of one form into the other without influencing the composition of the compound, is not in accordance with the behaviour of an isomorphous mixture.

The formation of the complex acid and its salts is analogous to the formation of metatungstic acid. A few reactions and the power of forming precipitates with peptones and organic bases are common to

both acids, they are also similar in crystalline form and in possessing an intensely bitter and strongly acid taste; the complex acid, however, is not affected by temperature or by mineral acids, and can be boiled with strong acids without decomposition. By prolonged dialysis of the complex acid, the phosphoric acid can be completely separated from the tungstic acid compound. The complex acid is partially dissociated in solution, and the phosphoric acid then passes through the membrane much more easily than the metatungstic acid.

The saturated solution of sodium metatungstate crystallises in skeleton forms which combine to form octahedra; sp. gr. = 4.04. At first the crystals have no action on polarised light, but they soon show cleavage lines and become optically active. The barium salt crystallises in the orthorhombic system, and is totally unlike the salt of the complex acid. Metatungstic acid dissolves in ether, and the solution has the same behaviour as that of the complex acid.

Metatungstic acid, $\text{H}_2\text{O}(\text{WO}_3)_4 \cdot 9\text{H}_2\text{O}$, has sp. gr. = 3.93. When heated at 50° , it is decomposed, and is no longer soluble in water; below 180° it is anhydrous. Phosphododecatungstic acid is not decomposed at 200° , and becomes anhydrous only at a red heat. Its stability and also its specific gravity is evidence for the complex character of the condensed compound.

The solubility of the acids and salts in water and ether and the specific gravities of the aqueous solutions are given, and also details of experiments on the lowering of the freezing points and raising of the boiling points of the solutions; the depression due to the condensed acid is much smaller than the sum of the depressions of its components. At the higher concentrations, the difference of the depressions for 1 gram of the complex acid is constant, at lower concentrations it is much smaller, this being due to the dissociation of the complex acid. The electrical conductivity of the complex acid is smaller than that of its components.

The author concludes that phosphododecatungstic acid is neither an isomorphous mixture nor a double salt, but must be considered as a complex acid.

E. C. R.

Chlorides of Zirconium. By FRANK P. VENABLE (*J. Amer. Chem. Soc.*, 1895, 17, 842—843).—The author had made repeated estimations of zirconium in the salt obtained by dissolving the hydroxide in hydrochloric acid, and recrystallising from the strong acid, with results that left no doubt that the compound was the pure tetrachloride; but having lately made some determinations of the chlorine as well, it now appears that Bailey was right in calling it an oxychloride. The probable formula is $\text{Zr}_3(\text{OH})_5\text{Cl}_7 + 5\text{H}_2\text{O}$.

L. DE K.

Action of Reducing Agents on the Nitroso-compounds of Ruthenium. By L. BRIZARD (*Compt. rend.*, 1896, 122, 730—732).—When the nitrosochloride, $\text{RuNOCl}_3 \cdot 2\text{KCl}$, is reduced by formaldehyde in presence of excess of alkali at 60° , it yields a black precipitate and a brown liquid, and when the latter is neutralised with hydrochloric acid, a brown precipitate separates consisting of oxides resulting from reduction of the nitrosochloride. When this pre-

precipitate is dissolved in hydrochloric acid, and the solution is concentrated, it yields small, red, optically active crystals which are readily separated from the accompanying chloride, $\text{Ru}_2\text{Cl}_5, 4\text{KCl}$, because they dissolve very slowly in cold water. The red crystals have the composition $\text{Ru}_2(\text{NO})\text{H}_4\text{Cl}_5, 3\text{KCl}$, and contain no water of hydration, but probably have the constitution $2\text{HCl}, \text{Ru}(\text{NO})\text{H}_2 \cdot \text{RuCl}_3, 3\text{KCl}$. With potassium hydroxide, they yield a pale brown precipitate, and 3 mols. of the hydroxide completely precipitate 1 mol. of the salt. The precipitate has the composition $\text{NO} \cdot \text{Ru}_2\text{H}_2\text{Cl}_2 \cdot \text{OH} + 2\text{H}_2\text{O}$. Ammonia has no effect on the solution of the red crystals in the cold, but, on heating, the liquid becomes pale yellow, and deposits a crystalline, yellow powder as it cools. Chlorine water converts the red salt into the original chloride, $\text{Ru}(\text{NO})\text{Cl}_3, 2\text{KCl}$, and when the red crystals are heated in hydrogen, a considerable quantity of ammonium chloride volatilises.

Stannous chloride reduces the nitrosochloride, and yields red crystals analogous in composition to the compound already described, but containing tin instead of potassium.

Ammonia reduces potassium rutheniate in the cold, and by the same method of subsequent treatment the same product is obtained as with formaldehyde. This reduction is analogous to the formation of potassium osmiamate by the action of ammonia on the osmate.

C. H. B.

Mineralogical Chemistry.

Alteration Products of Blende. By GIUSEPPE CESÀRO (*Ann. Soc. Géol. Belgique*, 1895, **22**, 217—224).—The transparent blende of Picos de Europa, Spain, is corroded and altered in places, presumably by the action of water containing carbonic anhydride. The soft, dull white, fibrous or amorphous material, after being dried at 100° , was analysed (I); the results correspond with the formula $2\text{ZnO}, \text{CO}_2, \text{H}_2\text{O}$ or $\text{ZnCO}_3, \text{Zn}(\text{OH})_2$, analogous to malachite: hydrozincite is usually given as $\text{ZnCO}_3, 2\text{Zn}(\text{OH})_2$, but the analyses vary.

	ZnO.	CO ₂ .	H ₂ O.	Total.
I.	72.15	19.77	8.08	100.00
II.	65.47	33.63	—	99.10

In the interior of the last substance, but never in contact with the unaltered blende, are kernels of a white, crystalline substance, with saccharoidal texture, and $H = 5$; the results of analysis are given under II, agreeing with ZnCO_3 .

The corrosion figures are described in detail, and the low degree of symmetry shown by them is discussed.

L. J. S.

Ochres. By GUSTAV GIN (*Compt. rend. Assoc. franç. Adv. Sci.*, 1895, **23** (1894), ii, 512—527).—The ochres are classed as yellow, red, and brown, the colour in each case being due to limonite,

earthy hæmatite, and a mixture of pyrolusite and ferric oxide respectively. Several analyses are given. Some ochres contain, in the clayey base, as little as 2—4 per cent. of ferric oxide, but generally only those with 9—10 per cent., or more, are of commercial value. The mode of occurrence and origin of ochres are described, as well as the methods of examining commercial samples. L. J. S.

Analyses of Argentine Minerals, &c. By FREDERICO SHICKENDANTZ (*Rev. Museo La Plata*, 1895, 7, 1—12).—Several analyses are given of soils, and of the impure material of salt deposits; many of the latter showing much sodium chloride, with sometimes sulphate and borate. The following are of interest: I. Salt from the Rio Negro district. [? Thenardite.] II. Yellow, friable sulphate, soluble in water; from east of Candado, prov. Catamarca. Also a trace of copper. [? Ihleite.] III. White salt from the volcano of Antofagasta, prov. Catamarca. [? Mendozite.] IV. Yellow salt, from the same locality as III.

	SO ₃ .	Na ₂ O.	Fe ₂ O ₃ .	Al ₂ O ₃ .	MgO.	H ₂ O.	Residue.	Total.
I.	54.00	43.93	—	—	—	0.86	0.48	99.27
II.	39.46	—	22.82	—	1.46	35.00	0.80	99.54
III.	37.19	4.62	—	15.49	—	38.60	4.60	100.50
IV.	34.93	little	14.99	—	—	43.44	5.87	99.23

L. J. S.

Basic Sulphate of Iron from Mount Morgan, Queensland. By THOMAS COOKSEY (*Records Australian Museum*, 1896, 2, 111—112).—This occurs as dull, compact, brown nodules in a matrix of iron oxide; the powder is yellow and crystalline. No water is given off below 175°; analysis gave

Fe ₂ O ₃ .	Na ₂ O.	K ₂ O.	SO ₃ .	H ₂ O.	Total.	Sp. gr.
49.13	4.43	3.88	33.31	9.96	100.71	3.107

The substance differs from jarosite in the proportion of potassium and sodium, and in being almost insoluble in water. L. J. S.

An Artificial Hydrated Magnesium Silicate. By LUCIEN L. DE KONINCK (*Ann. Soc. Géol. Belgique*, 1895, 22, 67—71).—The white, flaky, unctuous material, resembling powdered talc, which is formed by the action of magnesia solution (ammoniacal solution of magnesium and ammonium chlorides) on the glass of reagent bottles, gave, on analysis,

H ₂ O.	SiO ₂ .	MgO.	Al ₂ O ₃ .	Fe ₂ O ₃ (trace).	Total.
31.29	32.99	34.80	0.87		99.95

Calculating the alumina with the magnesia, the formula 18MgO, 11SiO₂, 35H₂O is deduced, or if the alumina be neglected, 3MgO, 2SiO₂, 6H₂O.

At 100°, about 17 per cent. of water (corresponding with 15H₂O in the first formula) is lost, which is reabsorbed from moist air. The

material has no action on polarised light. With different samples of glass, the substance formed had always the same amount of water. The composition is compared with talc, $3\text{MgO}, 4\text{SiO}_2, 4\text{H}_2\text{O}$, and serpentine, $3\text{MgO}, 2\text{SiO}_2, 2\text{H}_2\text{O}$.

It is suggested that serpentine and dolomite may have had their origin in the action of magnesia solutions on siliceous and calcareous rocks. (Compare this vol., ii, 116.) L. J. S.

A Silicate probably belonging to a New Mineral Species. By GIUSEPPE CESÀRO (*Bull. Acad. Belg.*, 1895, [3], 29, 508—510).—Along with the hexagonite of Edwards, St. Lawrence Co., N.Y., a colourless, or slightly rosy, opaline mineral of hardness 4·5 occurs; it is orthorhombic, with two cleavages parallel to planes of symmetry. Perpendicular to the better cleavage is an acute, negative bisectrix, with $2E = 83^\circ 30'$, the plane of the optic axis being parallel to the other cleavage. It is a silicate of magnesium with manganese and calcium, but contains neither iron nor aluminium. It is not attacked by acids; after the action of alkali carbonates, it leaves a residue of about 58 per cent., insoluble in acids. It is easily fusible. It differs from enstatite and anthophyllite. L. J. S.

Zeolites and the Substitution of various Substances for the Water which they contain. By GEORGES FRIEDEL (*Compt. rend.*, 1896, 122, 948—951; compare following abstracts).—When analcite is heated so that it loses water, it retains its original form and the refractive power is increased. At the ordinary temperature, the dehydrated mineral does not reabsorb water, but at about 100° it will reabsorb water from the air and return to its original composition. The tension of dehydration above 100° is of the same order as the pressure of aqueous vapour in the air, and for a given weight of mineral it depends on the area of surface exposed.

When chabazite, harmotome, and similar minerals are slowly heated, they retain their crystalline form, and their refractive power increases, whilst if rapidly heated, the crystals may break up, but the increase in refractive power is still recognisable; the variation in optical properties is proportional to the quantity of water expelled. It is known that these minerals reabsorb water from the air at the ordinary temperature; if, however, after dehydration, they are mixed with a few drops of water, combination takes place with great energy and development of heat, and at the same time a considerable quantity of air is liberated.

The water in the zeolites is not in chemical combination in the common sense of the word, and it can be replaced by various gases, and even by solids such as silica, without alteration in the crystalline form or optical properties of the minerals. Dehydrated chabazite, harmotome, heulandite, and analcite absorb ammonia in large quantity with great energy and development of heat, the quantity absorbed being independent of the nature of the zeolite and proportional to the quantity of water previously expelled. When exposed to moist air, the ammonia is gradually expelled, and its place is taken by water. In the case of analcite the analogy is very close; the ammonia, like

water, is not absorbed by the dehydrated mineral below 100° , and it is not displaced by atmospheric moisture at the ordinary temperature.

C. H. B.

A New Artificial Silicate. By GEORGES FRIEDEL (*Bull. Soc. fran. Min.*, 1896, **19**, 5—14).—This is formed, together with nephelite, when muscovite is heated at 500 — 530° in a solution (8—10 per cent.) of caustic soda; it is not formed when the temperature is too low, or when the solution is too dilute or contains silica. The colourless, transparent, orthorhombic crystals resemble olivine in habit, angles, and optical characters; twins on $m(110)$ are common. The material is easily attacked by hydrochloric acid. Analysis gave

SiO_2 .	Al_2O_3 .	Fe_2O_3 .	CaO .	Na_2O .	K_2O .	H_2O .	Total.
40.78	36.73	trace	0.15	15.40	1.88	4.93	99.87

This agrees with $15\text{SiO}_2, 8\text{Al}_2\text{O}_3, 6\text{R}_2\text{O} + 6\text{H}_2\text{O}$, which is an orthosilicate with water. On heating the crystals to bright redness, they lose water, but still remain limpid, there being a slight change in the optical characters, and a change of sp. gr. from 2.377 to 2.463. The crystalline form of the substance is therefore independent of the contained water.

L. J. S.

Analcite. By GEORGES FRIEDEL (*Bull. Soc. fran. Min.*, 1896, **19**, 14—18).—The behaviour of analcite ($\text{Na}_2\text{O}, \text{Al}_2\text{O}_3, 4\text{SiO}_2, 2\text{H}_2\text{O}$), when heated, is analogous to that of the new orthorhombic silicate (see preceding abstract), the water being lost with modification of the optical character and specific gravity, but without any change in the outward crystalline form. When analcite is heated, the crystals still remain more or less transparent, but become more strongly doubly refracting. Crystals from the Cyclopean Islands, when raised to a bright red heat, changed in sp. gr. from 2.277 to 2.179, and at a higher temperature they became isotropic, being then apparently permanently cubic. Some authors have considered that the double refraction of this mineral is connected with the loss of water, but this is not confirmed by the result obtained on heating analcite crystals in water to about 500° , as they remain unaltered and are still doubly refracting.

The water lost at various temperatures is given as: at 100° , none; 220 — 240° , 0.23 per cent.; 300 — 320° , total loss of 3.2 per cent.

L. J. S.

Natrolite from Moravia. By C. FRIEDRICH EICHLER (*Verh. k. k. geol. Reichsanst.*, 1895, 485—486).—Radially columnar aggregates of large crystals of white natrolite from the eruptive rocks at Palzendorf, Moravia, gave the following results.

SiO_2 .	Al_2O_3 .	Na_2O .	H_2O .	Total.
47.85	27.30	15.55	9.30	100.00
47.45	27.10	15.71	9.35	99.61

This agrees with the usual formula $\text{Na}_2\text{Al}_2\text{Si}_3\text{O}_{10} + 2\text{H}_2\text{O}$. Traces of calcium, but no iron, are present. Sp. gr. 2.229.

L. J. S.

Asbestos from Bosnia. By HEINRICH VON FOULLON (*Verh. k. k. geol. Reichsanst.*, 1895, 365—367).—In the weathered Triassic (Werfen) slates near Alilovci in N.W. Bosnia, are loose, irregular pieces of an asbestos-like mineral; it is also found in the associated limestone blocks, and is clearly of secondary origin. It is lavender-blue and finely fibrous. Analysis by L. Schneider gave

SiO ₂ .	Fe ₂ O ₃ .	FeO.	MgO.	CaO.	Na ₂ O.	K ₂ O.	Loss on ignition.		Total.
							CO ₂ .	—.	
54.10	15.76	7.33	12.60	1.44	5.40	0.45	0.09	2.81	99.98

It fuses easily to a black enamel. The mineral, as shown by its composition and outward appearance, is identical with the author's rhodusite from the Island of Rhodes (*Abstr.*, 1894, ii, 461). L. J. S.

[**Altered Biotite and Tremolite from Styria.**] By RICHARD CANAVAL (*Mitth. Ver. Steiermark*, 1895, 31, 39—43).—In a paper describing the occurrence and working of the cupriferous pyrites at Kallwang, in Upper Styria, are given the following analyses of minerals from the rocks bearing the ore. I is of the green material (vermiculite), originating by the chloritisation of the biotite, in a rock containing quartz, felspar, and carbonates. II is of colourless needles of tremolite, sp. gr. 2.952, from a rock containing also calcite, quartz, and a serpentine-like substance.

SiO ₂ .	Fe ₂ O ₃ .	FeO.	Al ₂ O ₃ .	MnO.	CaO.
31.782	4.075	17.751	27.534	2.764	1.735
51.246	—	4.449	—	1.605	13.354
		MgO.	K ₂ O.	H ₂ O.	Total.
		5.855	—	8.545	100.041
		24.985	1.754	2.586	99.979

L. J. S.

Dolomite from Graz. By J. A. IPPEN (*Mitth. Ver. Steiermark*, 1895, 31, 272—275).—Specimens of dolomite rock from the Schlossberg at Graz gave the following results on analysis.

CaCO ₃ .	MgCO ₃ .	FeCO ₃ .	Insol. (SiO ₂).	H ₂ O.	Total.
53.27	41.77	1.63	1.42	0.96	99.05
55.07	41.78	1.44	1.26	0.64	100.19
55.10	43.93	trace	0.30	not det.	99.33

L. J. S.

Disintegration of Granite in the District of Columbia. By GEORGE P. MERRILL (*Bull. Geol. Soc. Amer.*, 1895, 6, 321—332).—The rock when fresh is a grey, foliated and jointed, micaceous granite, analysis I; nearer the surface it is brown and friable, II; whilst still higher it is converted into sand and gravel, passing upwards into soil, III.

Ignition.	SiO ₂ .	TiO ₂ .	Al ₂ O ₃ .	FeO.	Fe ₂ O ₃ .	CaO.	MgO.
I. 1·22	69·33	not det.	14·33	3·60	—	3·21	2·44
II. 3·27	66·82	not det.	15·62	1·69	1·88	3·13	2·76
III. 4·70	65·69	0·31	15·23	4·39		2·63	2·64
	Na ₂ O.	K ₂ O.	P ₂ O ₅ .	Total.			
	2·70	2·67	0·10	99·60			
	2·58	2·04	not det.	99·79			
	2·12	2·00	0·055	99·765			

The disintegration has here been effected without any important change in composition beyond hydration and oxidation of the iron, and in this differs from the ordinary weathering of granite. The minerals, even in their smallest fragments, are in most cases quite fresh; and the disintegration is attributed to the unequal expansion of the minerals on hydration. Cold water extracts from the soil 0·0138 per cent., and hydrochloric acid 3·609 per cent. L. J. S.

The Smithville Meteoric Iron. By OLIVER W. HUNTINGTON (*Proc. Amer. Acad.*, 1894, **29**, 251—260).—Three masses, weighing about 7, 15, and 65 lbs. were ploughed up in 1892 near Smithville, De Kalb Co., Tennessee; they closely resemble the Cocke Co. iron. The iron shows a marked octahedral cleavage, and encloses nodules of troilite embedded in graphite and schreibersite; small crystals of cliftonite and perhaps also diamond are present. Analysis gave

Fe.	Ni.	Co.	Cu.	P.	Residue (mainly cliftonite).	Total.
91·57	7·02	0·62	trace	0·18	0·15	99·54

This analysis is compared with those of other irons from Tennessee and West Virginia, and it is pointed out that many of these may have originally formed part of the Cocke Co. fall. L. J. S.

Physiological Chemistry.

Gastric Digestion. By JOHN SJÖQUIST (*Chem. Centr.*, 1895, ii, 1127; from *Skand. Arch. f. Physiol.*, 5, 277).—For the author's method for estimating hydrochloric acid in gastric juice, see this vol., ii, 496.

Peptic digestion is stated to occur in two phases similar to those noticed in the inversion of cane sugar. W. D. H.

Action of Dilute Acids on Metabolism. By JAMES CRAUFURD DUNLOP (*J. Physiol.*, 1896, 20, 82—96).—The observations recorded

were made on human beings, and full details are given of the analyses of urine, fæces, and diet. After the administration of large doses of dilute mineral acids, the following phenomena were observed:—A great diuresis; a slight increase of the total, but not of the percentage, acidity of the urine; an increased excretion of nitrogen, which fell, not on the urea, but on the ammonia and extractives, and an increased excretion of sodium salts.

W. D. H.

Hæmoglobin and its Derivatives. By JEANNOT GEORGENBURGER (*Chem. Centr.*, 1895, i, 701—702; from *Pharm. Zeits. Russ.*, **34**, 102—104).—Hæmoglobin, hæmol, and hæmogallol were given with the food, and their value in nutrition gauged by the amount found in the fæces. The pigment after extraction was estimated by the spectroscope. 75 per cent. of hæmol was absorbed. The figures for the other substances are only approximate.

W. D. H.

Solubility of Carbonic Oxide in Solutions of Hæmoglobin: Dissociation of Carbonic Oxide Hæmoglobin. By C. GUSTAV HÜFNER (*Chem. Centr.*, 1895, ii, 308—309; from *Du Bois Reymond's Archiv*, 1895, 209—212, 213—214).—The absorption coefficient of carbonic oxide in solutions of hæmoglobin varies from 0.0213 at 19.5° to 0.0221 at 20.2°. It is therefore less than in pure water, where the absorption coefficient at 19.6° is 0.0233.

The dissociation constant of carbonic oxide hæmoglobin is about 33 times smaller than that of oxyhæmoglobin. Boehm's experiments (*Arch. exp. Path. Pharm.*, **35**, 16) on the toxic effects of certain alkaloïds are probably to be explained by an analogous increase in the difficulty of dissociation between them and the substance of nerve cells.

W. D. H.

Compounds of Fatty acids with Cholesterol in Blood-serum. By KARL HÜRTHLE (*Zeit. physiol. Chem.*, 1896, **21**, 331—359).—If blood-serum is first treated several times with alcohol, and then extracted with a mixture of alcohol and ether, two crystalline substances, melting at 43° and 77°, are obtained from the extract; on treatment with concentrated sulphuric acid, they show reactions similar to those of cholesterol, but in a modified manner. By treatment with alcoholic potash, they are decomposed into cholesterol and potassium soaps, the substances being really fatty acid compounds of cholesterol, namely the oleate and palmitate. The stearate was not found. It, however, and the others were made synthetically. The serum contains from 0.08 to 0.2 of the oleate, and from 0.006 to 0.008 of the palmitate.

Cholesterylic oleate crystallises in long, thin needles, melts at about 41°, and is soluble in ether, chloroform, and benzene, but only sparingly in alcohol; the rotatory power $\alpha_D = 18^\circ 48'$. The *palmitate* forms snow-white plates, melting at 77—78°.

W. D. H.

Formation of Lymph. By W. S. LAZARUS-BARLOW (*J. Physiol.*, 1896, **19**, 418—465).—In favour of the view that osmosis and increased filtration are the effective factors in producing the increased

outflow of lymph which follows the injection of a crystalloid into the blood, there are the following points:—

1. The evidence given by the lowering in specific gravity of the blood after injection of comparable quantities of molecular solutions of sodium chloride, glucose, and urea, which is found to vary directly as the initial rate of osmosis (through a copper ferrocyanide membrane) of the substance injected.

2. The fact that in a few cases the injection is followed by a temporary diminution in the outflow of lymph from a cannula placed in the thoracic duct.

3. The fact that the increased flow varies directly as the lowering of the specific gravity of the blood.

4. The fact that with large injections of weak sodium chloride solution in amounts bearing a constant ratio to the theoretical volume of the animal's blood, the ratio between the amounts of lymph formed before and after injection is practically a constant.

Against this view, there are following nine points:—

1. The initial fall in the sp. gr. of the blood after injection of concentrated solutions is frequently over compensated, and this occurs also after large injections of liquids having a smaller initial rate of osmosis than lymph or blood-plasma.

2. The fact that in most cases there is no initial diminution in the outflow of lymph.

3. The fact that in a few cases the injection may diminish the outflow, but the subsequent injection of another crystalloid may increase it.

4. The fact that after the water in the tissues has been lessened by an outflow of lymph, injection of a crystalloid with a lower initial rate of osmosis may lead to a greater increase of lymph than under normal circumstances.

5. The initial rate of osmosis of the lymph may be higher than that of the blood-serum.

6. The maximum outflow does not occur at the time of maximum intravenous pressure.

7. If the venous pressure is kept increased in a hind limb for an hour, or if the sciatic nerve is cut, there is in neither case an increase in lymph flow.

8. An initial diminution in lymph flow is produced by injection of an insoluble substance like lamp-black.

9. The assumption that the vessel walls are more nearly akin to a copper ferrocyanide membrane than to an animal membrane like peritoneum is improbable.

W. D. H.

Hygienic Studies on Copper. By KARL B. LEHMANN (*Chem. Centr.*, 1895, ii, 541—543; from *Arch. Hyg.*, **24**, 1—17, 18—72, 72—83).—Copper occurs in numerous articles of diet; quantitative results and methods of analysis are given. It is calculated that in our food we take about 20 milligrams of copper daily; but if preserves are much used, it may rise to over 300 milligrams per diem; more than 120 milligrams appears to be harmful.

W. D. H.

Absorption of Iron by the Organism. By JOHANNES TIRMANN (*Chem. Centr.*, 1891, ii, 407—408, 497—498; from *Pharm. Zeits. Russ.*, **34**, 403—405, 433—439).—Many observers believe that inorganic compounds of iron are not absorbed, but that organic compounds like hæmatogen (Bunge) or ferratin (Schmiedeberg) form the source of iron to the body. Artificial ferratin, prepared from alkali-albumin, and tartrate of iron and sodium, is not the same thing as the material separated from the liver by Schmiedeberg, and is not much more easily absorbed. Excretion of iron is normally chiefly performed by the mucous membrane of the intestine, only 10 per cent. leaving by the urine. Crystalline hæmoglobin, hæmogallol, and hæmatin are well absorbed, and the iron of the urine rises; these substances do good in cases of chlorosis. W. D. H.

Muscular Work and Glycogen. By JOSEF SEEGEN (*Chem. Centr.*, 1895, ii, 233; from *Centr. Physiol.*, **9**, 193).—From the examination of the blood entering and leaving a working muscle, the conclusion is drawn that the muscular glycogen is only in a very small degree the source of muscular work; the sugar of the blood is believed to be the most important substance from this point of view.

W. D. H.

Elimination of Carbonic Anhydride from Phosphorcarnic acid by Hydrolysis. By TH. RICHARD KRÜGER (*Zeit. physiol. Chem.*, 1896, **22**, 95—102).—By hydrolysis of phosphorcarnic acid (*Abstr.*, 1895, i, 313), carbonic anhydride is given off; in extracts of muscle, no other substance yields carbonic anhydride on hydrolysis with simultaneous oxidation by means of iron chloride. Phosphorcarnic acid is, therefore, regarded as the material which, during muscular activity, gives off carbonic anhydride without using up oxygen.

W. D. H.

Iodine Compounds in the Thyroid. By EUGEN BAUMANN and ERNST ROOS (*Zeit. physiol. Chem.*, 1896, **21**, 481—493).—The substance called thyriodin (this vol., ii, 263) is not destroyed nor dissolved by the action of heat, or sulphuric acid (1 in 10), or hydrochloric acid (10 per cent.). It can, therefore, be separated from the other constituents of the gland which dissolve in these reagents. It is not of the nature of a proteid or enzyme.

The proteids of the gland are an albumin with which the greater part of the thyriodin is combined, and a globulin with which a small part of the thyriodin is in combination. These, with a small amount of free thyriodin, are soluble in physiological saline solution. In the sheep's thyroid, the percentage of iodine in the dried organ varies from 0.9 to 1.5, and in the fresh organ from 0.26 to 0.44. Clinical and experimental evidence points to thyriodin as the active physiological material in thyroid extracts.

W. D. H.

Iodine in the Thyroid. By EUGEN BAUMANN (*Zeit. physiol. Chem.*, 1896, **22**, 1—17; compare this vol., ii, 263).—A large number of analyses of thyroids are given so far as the amount of iodine obtainable from them is concerned.

Human thyroids were examined after death from a large number of diseases; the cases of children are separated from those of adults; a number of the lower animals were also examined. The following table gives the main results.

		Dry weight of organ.	Iodine in 1 gram of organ.
Adult human thyroid; average of 26 cases, Freiburg....		8.2	0.33
" " " " 30 " Hamburg ...		4.6	0.83
" " " " 11 " Berlin		7.4	0.9
Children's " " 39 "		—	0 or traces

In dogs, little or no iodine was found; it was increased by feeding on dog biscuit. In other animals, it is much the same as in man. Iodine was found in calf's thymus.

W. D. H.

Action of Thyroidin. By ERNST ROOS (*Zeit. physiol. Chem.*, 1896, 22, 18—61; compare Abstr., 1895, ii, 516).—The activity of thyroids and thyroid extracts depends on the presence of thyroidin. This substance acts on the general system, on the thyroid gland itself, on cases of myxœdema and psoriasis, and on metabolism in the same way as thyroid extracts. Details of a large number of clinical cases are given.

W. D. H.

Nuclein and the Formation of Uric acid. By WILHELM WEINTRAUD (*Chem. Centr.*, 1895, ii, 234; from *Berlin klin. Woch.*, 32, 405—409).—Administration of thymus as food causes a large increase of uric acid in the urine. This is produced chiefly by the absorption of nuclein from the food, and only in a small degree arises indirectly by the diet increasing the number of leucocytes.

W. D. H.

Formation of Uric acid in Man. By WILHELM WEINTRAUD (*Chem. Centr.*, 1895, ii, 310—311; from *Du Bois Reymond's Archiv*, 1895, 382—385).—By feeding on cooked thymus, the basic nitrogen and the phosphoric acid of the urine are increased in the urine, but not in the fæces. Only a small part of the absorbed nuclein is changed into uric acid; it is probable that the uric acid is discharged into the intestine.

W. D. H.

Fibrin-ferment and Nucleo-proteid. By CORNELIUS A. PEKELHARING (*Chem. Centr.*, 1895, ii, 53; from *Centr. Physiol.*, 9, 102).—Halliburton and Brodie stated that there were numerous differences between fibrin-ferment and nucleo-proteid; the present communication shows that these are all susceptible of explanation.

W. D. H.

Note by Abstractor.—Halliburton and Brodie have more recently (*J. Physiol.*, 18, 306) and independently arrived at the same conclusion, namely that fibrin-ferment is a nucleo-proteid.—W. D. H.

Chemistry of Mitosis. By L. HEINE (*Zeit. physiol. Chem.*, 1896, **21**, 494—506).—Lilienfeld concludes from microchemical work that in the dividing nucleus of cells, free nucleic acid is liberated. In the present research, this conclusion is questioned; the only change that occurs is one in the physical groupings of the chromatic filaments.

The microchemical reactions described for distinguishing between free nucleic acid and its proteid compounds, and between acidophile and basophile reactions as tested by aniline dyes, are not trustworthy. According to the previous treatment of the objects (method of hardening, &c.), any variety of selective colouring can be obtained. The results described are, therefore, chiefly of histological rather than of chemical interest.

W. D. H.

Rennin and Milk Clotting. By ARTHUR EDMUNDS (*J. Physiol.*, 1896, **19**, 466—476).—A small quantity of a milk-curdling ferment can be obtained from many tissues besides the stomach, namely, testis, liver, lung, muscle, kidney, spleen, thymus, thyroid, brain, blood, small intestine, ovary.

There is no evidence that casein can be reconverted into caseinogen and re-coagulated by rennin, the apparent re-coagulation described by Peters (*Preisschrift Rostock*, 1894) being probably due to calcium salts present in the rennet extract.

Peptone has a marked retarding effect on coagulation, which may be partly neutralised by calcium chloride.

Casein is soluble in ammonium oxalate solution without being reconverted into "caseinogen."

Grimaux's "colloïde aspartique" has no coagulating effect on milk.

W. D. H.

Effect of Borax on Milk Curdling. By F. J. ALLEN (*Lancet*, 1896, **1**, 1516).—Milk containing one-tenth of its volume of cold saturated solution of borax will not curdle with rennet; but this property is restored by calcium chloride. Boric acid, on the other hand, hastens rather than hinders rennet activity. The conclusion that the action of borax is due to the base rather than to the acid was confirmed by the discovery that sodium hydrogen carbonate has the same action as borax, if one-sixth of a 5 per cent. solution is added to the milk. This also is neutralised by calcium chloride.

W. D. H.

Absorption and Excretion of Lime. By J. G. REY (*Chem. Centr.*; 1895, ii, 55—56, and 837; from *Arch. exp. Path. Pharm.*, **35**, 295—305; and *Deut. med. Woch.*, **21**, 569—572).—On subcutaneous injection of lime and calcium salts in dogs, a small part (12—13 per cent.) appears in the urine, the remainder being excreted into the intestine, especially the large intestine.

In rickets, the absorption of calcium compounds from the intestine is lessened, although this can hardly be considered the cause of the disease. In osteomalacia, the calcium in the urine suddenly sinks about the twelfth day; this is possibly an indication of commencing repair.

W. D. H.

Pentosuria. By ERNST L. SALKOWSKI (*Chem. Centr.*, 1895, ii, 177—178; from *Berlin klin. Woch.*, 32, 364).—Two new cases of pentose in the urine are described. The abnormal constituent was found for a considerable time, but no cause in the way of diet could be found to account for it. It is absent from diabetic urine. Hammarsten separated a pentose from the nucleo-proteid of the pancreas; thus pentose may originate within the body, and if oxidation processes are lessened, may leave in the urine as such. W. D. H.

Milk Sugar in the Urine after Child-birth. By F. A. LEMAIRE (*Zeit. physiol. Chem.*, 1896, 21, 442).—The presence of lactose in the urine of women after delivery has been often mooted, and a certain result is now arrived at by employing Baumann's benzoic chloride method of separating carbohydrates. The osazones of the carbohydrates were then prepared.

Baisch's result that normal urine contains glucose and a dextrin-like substance is confirmed; isomaltose was also found; and in fifteen cases after child-birth, but not before delivery, lactose was found too. The figures given are as follows:—

	Ante partum.	Post partum.
Glucose, per cent.	0.004 to 0.008	0.007 to 0.014
Isomaltose, per cent. ...	0.001 „ 0.002	0.002 „ 0.0035
Lactose, per cent.	none	0.01 „ 0.04

W. D. H.

The Relationship of Levulinic acid to Acetonuria. By WILHELM WEINTRAUD (*Chem. Centr.*, 1895, i, 292; from *Arch. exp. Path. Pharm.*, 34, 367—373).—Levulinic acid is regarded as the intermediate parent substance between the proteids of the body and the acetone and acetoacetic acid of the urine of diabetic patients. It is especially a decomposition product of the nuclei of cells. It is not toxic, although Jaksch has stated that it is. W. D. H.

Excretion of Uric acid and Xanthine Bases by the Fæces. By WILHELM WEINTRAUD (*Chem. Centr.*, 1895, ii, 54—55; from *Centr. Klu. Med.*, 16, 433—436).—In a case of leucæmia the rise of uric acid in the urine was found not to correspond with the increased number of leucocytes; here, however, an enormous increase in the xanthine bases of the fæces was found. These bases always occur in the fæces and are regarded as a true excretion, not as food residues. W. D. H.

Solubilities of Uric acid in Urine. By FRED. J. SMALE (*Chem. Centr.*, 1895, ii, 833—834; from *Centr. Physiol.*, 9, 385—390).—At 40°, uric acid is soluble in 2400 parts of water, which is more than has been found hitherto. In solutions of sodium chloride, the solubility is less; this varies with temperature, and tables of the solubility of uric acid in solutions of this and other salts are given.

There is more uric acid in the urine than is indicated by the silver method, as a part of the compound is held in solution by the urea present. W. D. H.

The Precipitation of Urates within and without the Body.

By C. MORDHORST (*Chem. Centr.*, 1895, ii, 795—797; from *Centr. inn. Med.*, **16**, 841—847).—This paper is a discussion as to the relationships of the reactions of the various juices and secretions of the body, and how changes in these reactions may determine the precipitation of uric acid or urates as in an attack of acute gout.

W. D. H.

Alloxuric Substances in the Urine of Children in Disease.

By ADOLF BAGINSKY and PAUL SOMMERFELD (*Zeit. physiol. Chem.*, 1896, **21**, 412—421).—Seven cases of diseases in children are described; the following points were noted in their urine.

1. Nephritis after whooping cough. Alloxuric bases (A) increased, uric acid (B) diminished; total alloxuric substances (C) increased.

2. Nephritis and endocarditis; (A) increased, (B) diminished, (C) normal.

3. Scarlatina, (A) increased; (B) normal; (C) increased.

4. Ditto (A) „ (B) diminished; (C) normal.

5. Diphtheria, (A) „ (B) normal; (C) increased.

6. Ditto (A) „ (B) diminished; (C) diminished.

7. Diabetes (A) „ (B) increased; (C) increased.

W. D. H.

Indican, Indoxylsulphuric acid, and Conjugated Glycuronic acids in the Urine.

By A. DAIBER (*Chem. Centr.*, 1895, ii, 309; from *Schweiz. Woch. Pharm.*, **33**, 229—236).—A number of urines were analysed; some contained only indoxylsulphuric acid, others only indican, and others sugar and indoxylglycuronic acid. The latter substance is lævorotatory, and so influences the rotation as well as the reducing power of the urine in the estimation of the sugar.

W. D. H.

Poisoning with Potassium Chlorate.

By KURT BRANDENBURG (*Chem. Centr.*, 1895, ii, 685; from *Berlin Klin. Woch.*, **32**, 583—586).—The blood of a suicide who took 40 grams of potassium chlorate was rich in methæmoglobin; the corpuscles were broken up. There was icterus, and during the first two days methæmoglobin passed into the urine. The total solids of the blood were lessened.

W. D. H.

Physiological Action of Cadmium.

By CESARE PADERI (*Chem. Centr.*, 1895, i, 794; from *Arch. Farm. terapeutica*, **3**).—Cadmium paralyses the central nervous system; it extends centrifugally, the muscles being influenced last. The effect on the heart is produced partly on its nerves, partly on its muscular substance. Cadmium is an antiseptic.

W. D. H.

Physiological Action of Thallium.

By ANTONIO CURCI (*Chem. Centr.*, 1895, ii, 999; from *Ann. Chim. Farm.*, **22**, 441—449).—Thallium and its salts depress the heart and circulation in frogs. In dogs, the pulse becomes slower, although the pressure rises as with alkalis generally. After a dose of curare, large enough to affect the heart and vaso-motor nerves, thallium, like potassium, causes a rise of blood pressure.

W. D. H.

Toxicity of Acetylene. By RUDOLF ROSEMAN (Chem. Centr., 1895, ii, 998—999; from *Arch. exp. Path. Pharm.*, **38**, 178—196).—Acetylene, prepared from calcium carbide, contained hydrogen phosphide and sulphide. This impure product is less poisonous than coal gas. It produces no change in the blood; it causes sleepiness, the respiration becoming slow, deep, and finally dyspnoeic. Some animals vomited. Its action appears to be on the nervous system.

W. D. H.

Physiological Action of Ureides. I. Alloxan, Alloxantin, and Parabanic acid. By VALERIO LUSINI (Chem. Centr., 1895, ii, 311, 727—728, 838; from *Ann. Chim. Farm.*, **21**, 241—257, **22**, 341—351, 385—394).—Alloxan increases nervous irritability and acts also, but with less intensity, on the muscles. It leaves the body in the urine as alloxantin and parabanic acid. Alloxantin behaves like alloxan in its physiological action, but is especially poisonous to cold blooded animals. The blood shows strongly reducing properties; this is not produced by the other two substances. Given by the stomach, it appears in the urine chiefly as parabanic acid, and in smaller quantities as dialuric acid, murexide, and alloxantin itself. Parabanic acid lessens the secretion of the skin, produces midriasis, increases reflexes, and finally kills in a state of torpor, the heart stopping in diastole.

All these substances act on the central nervous system, producing first stimulation, then paralysis. Alloxan is the most, and parabanic acid the least poisonous.

W. D. H.

Physiological Action of Gentisic acid. By ALEXIS LIKHATSCHEFF (*Zeit. physiol. Chem.*, 1896, **21**, 422—441).—Homogentisic (2:5-dihydroxyphenylacetic) acid is the substance formed in urine in cases of so-called alcaptonuria. Experiments were in the present research made on dogs; it is almost harmless, and appears as such in the urine, and does not unite in the organism with sulphuric acid. Gentisic acid, however, is poisonous, and unites with sulphuric acid, giving rise to an increase of ethereal sulphates in the urine; part, however, remains unaltered, and is excreted as such. Quinol is strongly toxic and is excreted in the form of ethereal sulphate alone.

In alcaptonuria there is no rise in the excretion of ethereal sulphates, and so no gentisic accompanies the homogentisic acid.

W. D. H.

Physiological Action of Caffeine and Theobromine. By MANFREDI ALBANESE (Chem. Centr., 1895, ii, 234—235; from *Arch. Exp. Path. Pharm.*, **35**, 449—466).—Caffeine given to dogs leaves the body in the urine as a methylxanthine; this, however, is only an intermediate product, since if it is itself injected subcutaneously, very little is found in the urine. This methylxanthine is probably identical with heteroxanthine. Theobromine is partly decomposed in the same way.

W. D. H.

Alkaloids of Hydrastis Canadensis. By KUNO VON BUNGE (Chem. Centr., 1895, i, 1173—1175; from *Arb. Pharm. Inst. Dorpat.*, **11** and **12**).—Hydrastinine gives precipitates which are mostly yellow,

and some crystalline, with the various precipitants of alkaloids. Potas-sio-mercuric iodide will detect it when diluted with 100,000 parts of water. It has no effect on red corpuscles; it paralyses the peripheral nerves and muscles. Small doses do not affect the heart, but large ones paralyse the vagus. The kidney vessels are dilated. The fatal dose for cats is 0.3 gram per kilo. of body weight. It leaves the body unchanged, principally by the urine.

Canadine hydrochloride and sulphate were also examined. They are precipitable by a large number of reagents. Outside the body canadine causes a change in the pigment of the red corpuscles into methæmoglobin; internally it does not show this property, but increases the disposition of the blood to deposit para-hæmoglobin crystals. It acts paralytically on the heart, and in larger doses on the brain and spinal cord, and it increases intestinal movements. The fatal dose for cats is 0.2 gram per kilo. of body weight. It is not wholly absorbed from the alimentary canal, but that which is, leaves the body as oxalic acid in the urine.

W. D. H.

Chemistry of Vegetable Physiology and Agriculture.

Inversion of Cane Sugar by means of Micro-Organisms.

By CLAUDIO FERMI and GIUSEPPE MONTESANO (*Chem. Centr.*, 1895, ii, 712—713; from *Centr. Bakt. und Parasitenk.*, 1, 482—487, 542—546). —Of 70 species of micro-organism with which the authors have worked, only the following bring about inversion when added to a bouillon culture containing cane-sugar, *Bacillus megaterium*, *Proteus vulgaris*, *Bacillus fluoresc. liquef.*, white yeast, rose yeast. Cholera vibrios and *Vibrio Metschnikovii* are uncertain in their action.

When the bouillon is rendered alkaline with excess of magnesia *Bacillus fluoresc.*, *Proteus* and rose yeast lost their inverting powers. Most of the organisms retain this power in slightly acid solutions, one exception to this is *Vibrio Metschnikovii*. Invertase is also formed when glycerol takes the place of cane sugar in the bouillon, but is not formed by certain bacteria in peptonised bouillon, nor in bouillon containing racemic acid. The beginning of the formation of invertase varies with the culture medium, and also with the special organisms; it usually, however, takes place two to three days after inoculation. In bouillon cultures containing cane sugar, no invert sugar can be detected during the first two days, although active invertase can be shown to be present.

Invertase is also formed in a medium containing no proteid matter. In a pure 5 per cent. glycerol medium, *Aspergillus niger* and *Pencilium glaucum* alone yield invertase. The amount of invertase formed by mould fungi is always greater than that formed by Schizomycetes, and may be increased or diminished by means of heat. The invertase obtained from mould fungi may be heated to 100° for over an hour

without being destroyed. Acids, especially inorganic acids, and alkalis, especially potash, rapidly destroy the enzyme.

J. J. S.

Biochemical Preparation of Sorbose. By GABRIEL BERTRAND (*Compt. rend.*, 1896, **122**, 900—903).—Sorbose does not exist ready formed in the juice of *Sorbus aucuparia*, *S. intermedia*, or *S. latifolia*. The juice of these plants rapidly ferments; all the glucose disappears, and a corresponding quantity of alcohol is formed, but when fermentation is complete the liquid contains no sorbose. At this point, the surface of the liquid is filled with *Saccharomyces vini*, which oxidises the alcohol, and often this is followed by *Penicillium glaucum* and other moulds, which completely alter the juice but without producing sorbose. Sometimes, however, small, reddish flies are attracted to the liquid, and it is then seen that the supernatant film becomes gelatinous and consistent, eventually loses its translucidity, and dries up with a greenish colour. The liquid then contains large quantities of sorbose.

The conversion of the sorbitol into sorbose is brought about by a microbe of $2\ \mu$ to $3\ \mu$ long, about $0.5\ \mu$ broad, which is introduced into the juice by the red fly previously mentioned. In order to obtain this ferment, a mixture of wine and vinegar or red wine with twice its volume of water is left exposed to the air in different places, until the microbe begins to develop its gelatinous colonies, thicker and more opaque in the central portions, which very soon become confluent, so that the membrane can be removed in one piece. The ferment is introduced into the juice of a fruit or into an artificial nutrient fluid containing sorbitol. In the case of the fruit juice, alcoholic fermentation must first be completely finished, and the liquid carefully filtered. The artificial nutrient fluid may be a solution of yeast or a 1 per cent. solution of peptone mixed with inorganic salts. Fermentation is allowed to go on in shallow vessels at 25° until the reducing power of the liquid with reference to Fehling's solution no longer increases.

C. H. B.

Nitrates in Seedlings. By ERNST SCHULZE (*Zeit. physiol. Chem.*, 1896, **22**, 82—89; compare *Abstr.*, 1895, ii, 84).—The occurrence of nitrates in various etiolated seedlings has been noted previously, the nitric acid being formed from proteid matter during germination. The circulating nitrogen, however, is generally and mostly in the form of amides, and in the cases of *Lupinus angustifolius*, *L. albus*, *Vicia sativa*, *Ricinus communis*, and *Zea Mays* the search for nitrates during the first 14 days of growth gave negative results.

W. D. H.

Saps. By ALEXANDRE HÉBERT (*Bull. Soc. Chim.*, [3], **13**, 927—932).—The author has examined the saps of certain varieties of plants, namely, of a creeper of the Ampelocissus tribe from the French Congo, of the Banana tree (*Musa paradisiaca*), and of the vine (*Vitis vinifera*). The first is characterised by containing a comparatively large percentage of iron.

The sap of *Musa paradisiaca* contains tannin, gallic acid, acetic acid, sodium chloride, and salts of calcium, potassium, and aluminium.

The sap of the vine, on treatment with lead acetate, yields a substance giving, with phenylhydrazine, an osazone melting at 205° , which is the melting point of glucosazone. J. F. T.

Some Constituents of Nettles. By ERCOLE GIUSTINIANI (*Gazzetta*, 1896, 26, i, 1—7).—The author has examined *Urtica urens* and *Urtica dioica* with the object of determining to which constituents they owe their powerful hæmostatic action. No alkaloids could be extracted from the plants, either before or after flowering. The freshly expressed juice of the nettles collected before flowering has occurred gives off nitrous vapours when heated or distilled, but the amount of such vapours evolved diminishes greatly as the plant reaches maturity, and the aqueous extract of the dried plant gives off no nitrous vapours on distillation; this behaviour is probably due to the simultaneous presence of formic acid and nitrates in the plant juices. The nettle probably contains a glucoside, which readily undergoes hydrolysis with formation of one or more volatile acids.

W. J. P.

Chemical Characteristics of Bilberry Juice. By W. NACKEN (*Chem. Centr.*, 1895, 66, 1084; from *Forsch. Ber. Lebens. Hyg.*, 2, 350—361).—The colouring matter is best isolated by treating the juice, which has been previously nearly neutralised with soda, with hide powder. The hide powder takes up the colouring matter from the juice in the course of two days, and is then collected and well washed with water; the colouring matter is extracted with dilute hydrochloric acid, and may be precipitated from the solution by dilute soda. When moist, it forms an indigo-blue paste, but when dry, a bluish-black mass with a reddish lustre. It dissolves in mineral and organic acids, but is insoluble in water, alcohol, ether, chloroform, or benzene. The solution changes to dark brown when treated with ferric chloride, to violet with copper sulphate or zinc chloride, and to indigo-blue with lead acetate. It reduces Fehling's solution, and is decomposed by hot concentrated sulphuric acid, a compound, $C_{14}H_{14}O_7$, being thrown down when the dark red solution thus obtained is diluted with water. Nitric acid oxidises the colouring matter to picric and oxalic acids. It slowly decomposes on standing; and its acid solution, when boiled, evolves 4.9 per cent. of carbonic anhydride; it is readily acetylated, and apparently has the composition $C_{10}H_{12}O_8$. When chlorine is passed into the juice, a bright grey, amorphous precipitate is obtained. This contains 24.77 per cent. of chlorine, and is sparingly soluble in water but readily in alcohol, has acid properties, reduces Fehling's solution, and can readily be benzoylated.

Considerable quantities of citric and malic acids are present in the juice, but no tartaric or oxalic acid. The carbohydrates present include glucoses, pentoses, and inositol.

The fermentation products of the juice include aldehyde, and capric, propionic, valeric, and butyric acids. J. J. S.

Nitric acid in the Waters of the Seine and its Chief Tributaries. By J. J. THÉOPHILE SCHLOESING (*Compt. rend.*, 1896, 122, 699—703).—The author has continued his investigations of the quan-

tity of nitrates in the waters of the Seine, Marne, Yonne, and Oise (Abstr., 1895, ii, 286), and has made estimations throughout 1895. The variations are approximately the same in all four rivers; the proportion of nitric acid is at a minimum (3 to 4 milligrams per litre) in July, August, and September, gradually increases until it reaches a maximum (9 to 10 milligrams per litre) in January or February, and then decreases again. The proportion of nitric acid has no definite relation to the volume of water passing down the stream. The maximum corresponds with a period of the year when surface drainage is small and the activity of aquatic plants is low; the minimum corresponds with the season when the activity of aquatic vegetation is at its maximum. C. H. B.

Apparatus for estimating the Water-holding Power of Soils. By J. L. BEESON (*J. Amer. Chem. Soc.*, 1895, **17**, 769—771). —The apparatus looks, at first sight, like a nitrometer. Inside the wider tube is placed a perforated disc, which is afterwards covered with filter paper, the disc being connected with a pressure tube, bent downwards at its upper end. The soil to be tested is placed on the disc, and by raising the narrow tube of the apparatus a known volume of water is forced through the soil; the tube is then lowered, and the volume of water again measured. The difference in the two readings represents the water absorbed by the soil. L. DE K.

Analytical Chemistry.

Estimation of Hydrogen by means of Palladious Chloride.

By EDWARD D. CAMPBELL and E. B. HART (*Amer. Chem. J.*, 1896, **18**, 294—298).—A freshly prepared, nearly neutral 1 per cent. solution of palladious chloride completely absorbs small quantities of hydrogen in the course of two hours. No advantage is gained by using a stronger solution, whilst the absorption is retarded if the solution be strongly acid. A. L.

Estimation of Free Hydrochloric acid in Gastric Juice.

By JOHN SJÖQUIST (*Zeit. anal. Chem.*, 1896, **35**, 240—253; from *Skandinav. Archiv. Physiol.*, **5**, 277).—The author has somewhat modified his process (*Abstr.*, 1893, ii, 433) by converting the barium chloride, resulting from the action of the gastric juice on barium carbonate, into chromate, and estimating the latter by Zulkowsky's iodimetric method. 10 c.c. of the gastric juice is mixed in a platinum basin with 0.5 gram of barium carbonate, evaporated to dryness and gently incinerated. The ash is exhausted with boiling water, and the solution is mixed with ammonium acetate, acetic acid, and ammonium chromate. The precipitate is washed free from soluble chromates, diffused in 10 c.c. of water, and treated with 2 c.c. of 30 per cent. potassium iodide solution and 5 c.c. of hydrochloric acid,

and the liberated iodine is titrated with thiosulphate. Since 6 atoms of iodine are liberated for each 4 mols. of hydrochloric acid, a thio-sulphate solution of about 31 grams per litre corresponds with 3 milligrams of hydrochloric acid per c.c. Objections to the method are discussed.

M. J. S.

Detection of Fluorine in Beer. By RUDOLF HEFELMANN and PAUL MANN (*Chem. Centr.*, 1895, i, 1081; from *Pharm. Centr. Halle*, 16, 249—250).—A crystalline compound containing 85 per cent. of silicon fluoride and 15 per cent. of ammonium fluoride is now largely used as an antiseptic. To detect fluorides in beer, 500 c.c. of the sample (freed from carbonic anhydride) is mixed with 1 c.c. of a mixture of equal parts of 10 per cent. calcium and barium chloride solutions, and then with 0.5 c.c. of 20 per cent. acetic acid. After adding 50 c.c. of 90 per cent. alcohol, the whole is left for 24 hours to allow the calcium fluoride and barium silicofluoride to settle. The precipitate is collected, and at once dried in a platinum crucible. The fluorine is now tested for, in the usual way, by heating with 1 c.c. of sulphuric acid, and noticing the action of the fumes on a watch glass.

L. DE K.

Detection of Fluorine in Wine. By G. NIVIÈRE and A. HUBERT (*Chem. Centr.*, 1895, ii, 251; from *Mon. scient.*, [4], 9, 1).—One hundred c.c. of the sample is rendered alkaline with aqueous soda, and boiled for a few minutes with 2—3 c.c. of a 10 per cent. solution of calcium chloride. The precipitate is collected on a filter and, after ignition, the residue is mixed with one-third of its weight of precipitated silicic acid. The mixture is then heated with a mixture of equal parts of ordinary and fuming sulphuric acid in a small test-tube connected with a small-pattern nitrogen bulb. The presence of 1 gram of ammonium fluoride in 100 litres of wine may be detected by the cloudiness of the water in the bulb-apparatus. The contents of the bulbs may then be filtered, and precipitated by means of a solution of potassium acetate in very weak alcohol; a precipitate of potassium silicofluoride is thus obtained, which may be weighed.

L. DE K.

Estimation of Sulphur in Refined Copper. By G. L. HEATH (*J. Amer. Chem. Soc.*, 1895, 17, 814—821).—Ten grams of the sample is dissolved in a mixture of 60 c.c. of nitric acid (sp. gr. 1.42) and 15 c.c. of hydrochloric acid (sp. gr. 1.20), and the whole is evaporated to dryness. To ensure the complete oxidation of the sulphur, the mass is again treated with 50 c.c. of nitric acid, and evaporated to dryness; this operation is then once more repeated. The residue is dissolved in 300 c.c. of water, adding, if necessary, a little nitric acid. After filtering, the liquid is diluted to about 600 c.c., and then subjected to electrolysis, a sheet of platinum of 4—5 in. serving as the negative electrode, whilst a small platinum foil serves as the positive one. A current equivalent to two 16-candle power lamps coupled in parallel will deposit the copper over night. The liquid free from copper, or nearly so, is evaporated with addition of a little sodium carbonate; when dry the mass is gently ignited to

expel any ammonium nitrate. The evaporations are best done with the aid of a spirit lamp to avoid sulphurous fumes. The mass is now freed from nitric compounds by repeated evaporation with hydrochloric acid, and the sulphuric acid is finally precipitated as usual with barium chloride. It is advisable to make a blank experiment to learn exactly the amount of sulphuric acid contained in the reagents used. If the copper be not first removed by electrolysis, it will exercise a decided solvent action on the barium sulphate. If lead is present, traces of lead sulphate may remain on any of the filters, but the sulphuric acid may be easily recovered by boiling with a solution of sodium carbonate.

L. DE K.

Estimation of Sulphur in roasted Copper Ores and Cupriforous Pyrites. By HARRY FREDERICK KELLER and MAAS (*Chem. Centr.*, 1895, ii, 412; from *J. Franklin Inst.*, 1895, 286).—0.5 gram of the finely powdered sample is introduced into a nickel crucible containing 5–6 grams of potassium hydroxide in a state of fusion, and when the mass has become red hot, 1 gram of sodium peroxide is added; the oxidation is complete after five minutes. The mass contains sulphate, which is then estimated as usual. If excess of sodium peroxide is used, a little copper dissolves, which interferes with the volumetric estimation of the sulphuric acid.

L. DE K.

The Evolution Method for the Estimation of Sulphur in White Cast-iron. By FRANCIS C. PHILLIPS (*J. Amer. Chem. Soc.*, 1895, 17, 891–900).—The author has modified this method so as to prevent loss of sulphur. The sample of iron is dissolved in hydrochloric acid of 1.12 sp. gr. in a current of carbonic anhydride. When the action becomes retarded, heat is applied. The hydrogen is passed through a porcelain combustion tube heated to redness, and containing a roll of platinum foil, 8 in. long. The delivery tube from the evolution flask must reach as far as the platinum, so that any oily drops which distil over may drop on it. The liquid in the flask is finally kept gently boiling until no more oily matter passes over, which may take over two hours. After escaping from the porcelain tube, the gas is absorbed in dilute hydrochloric acid containing bromine placed in a nitrogen flask. It is then again passed through a litre of the same solution contained in a large bottle. The sulphur is finally weighed as barium sulphate. The test-analyses show the great loss of sulphur taking place when using the old method, but they agree very well with those obtained by Blair's aqua regia method.

L. DE K.

Estimation of Sulphur in Pyrites. By GEORG LUNGE (*J. Amer. Chem. Soc.*, 1895, 17, 772–775).—A final reply to Gladding, upholding his own process. The author again states that when following the proper directions, the ferric hydroxide retains no sulphuric acid. The trace of barium chloride occluded by the barium sulphate is counterbalanced by the slight solubility of the sulphate in strongly acid liquids.

L. DE K.

Detection of Free Sulphuric acid in Leather. By BALLAND and MALJEAN (*Chem. Centr.*, 1895, i, 1045; from *Rep. Pharm.*, 1895, 108).—The sample is dried at 80°, powdered, and extracted with alcohol. The filtrate is neutralised with potassium carbonate, evaporated to dryness, and the residue ignited; it is then tested for a sulphate. If a quantitative estimation is desired, 10 grams of the sample must be extracted with alcohol in a Soxhlet's apparatus. Estimating the sulphates by ignition before and after neutralising with potassium carbonate gives less trustworthy results.

L. DE K.

Arsenic in Glycerol. By G. E. BARTON (*J. Amer. Chem. Soc.*, 1895, 17, 883—890).—Five grams of the sample is heated with 5 c.c. of a mixture of 30 parts of sulphuric acid and 1 part of nitric acid, with constant stirring, until a dry, charred mass is left; after cooling, 15 c.c. of water is added, and the mixture vigorously boiled to expel sulphurous anhydride. The liquid is then filtered, and the residue boiled twice with water to ensure the complete extraction of the arsenic. The liquid is then tested by the method proposed by Sanger for the estimation of arsenic in wall paper, which consists in comparing the arsenical mirrors yielded by the sample with those obtained from known amounts of arsenious oxide. In order to obviate the necessity of using chemically pure zinc and acid in the constant hydrogen generator, the author passes the gas through a solution of silver nitrate to free it from arsenic. In other respects, Sanger's instructions are followed.

L. DE K.

Estimation of Graphite in Pig-iron. By PORTER W. SHIMER (*J. Amer. Chem. Soc.*, 1895, 17, 873—876).—The higher results obtained by dissolving the sample in hydrochloric acid instead of nitric acid, have been ascribed to a supposed oxidation of the graphite by the latter acid.

The author has now distinctly proved that, on dissolving iron in hydrochloric acid, a not inconsiderable amount of titanium carbide remains, the carbon of which then counts as graphite. This compound is dissolved by nitric acid; the nitric acid process should therefore be used.

L. DE K.

Estimation of Lime by an Alcoholic Solution of Potash-soap. By L. SZYFFER (*Chem. Centr.*, 1895, i, 1082; from *Böhm. Zeit. f. Zuck. Ind.*, 19, 408).—This well-known method is very suitable for estimating lime in saccharine liquids. The soap solution should be made of such a strength that 1 c.c. equals 0.001 gram of CaO, and 150 c.c. of the sample should not require more than 20 c.c. of the soap; if it does, it must be suitably diluted. When testing acid juices, these should be first neutralised with ammonia. The lather should be permanent for at least five minutes. Sometimes it will be necessary to heat to 40° to promote the action.

L. DE K.

Solubility of Barium Sulphate. By C. REMIGIUS FRESSENIUS and E. HINTZ (*Zeit. anal. Chem.*, 1896, 35, 170—183).—In consequence of the wide discrepancies between the statements of various

authorities, the authors have made an extensive series of experiments with such liquids as are likely to occur in the course of sulphuric acid or barium estimations. The experiments were made by forming small amounts of barium sulphate from standard solutions of baryta and sulphuric acid in large volumes of the solvent, and observing the limit at which turbidity began to appear. Such mixtures as remained clear were, after 24 hours, divided, and treated with considerable excesses of barium chloride and sulphuric acid respectively, so as to imitate the conditions occurring in actual estimations. In all cases these additions diminished the solubility, so that with excess of sulphuric acid present 400,000 parts of each of the solvents given below were required to dissolve 1 part of barium sulphate. The other results obtained may be summarised as follows: the numbers given are the volumes in cubic millimetres requisite for retaining in clear solution 1 milligram of barium sulphate for at least 24 hours.

Water 100,000; water with excess of barium chloride 400,000. An 8 per cent. solution of ammonium chloride, 10,000; the same, + barium chloride, 50,000. A 2.3 per cent. solution of ammonium chloride, 22,000; the same with barium chloride, 80,000; a 2.3 per cent. solution of sodium chloride gives slightly lower solubilities than ammonium chloride. Nitric acid of 7—8 per cent., 7,300; the same with barium chloride, 33,000. Hydrochloric acid of 7—8 per cent. almost the same numbers as with nitric acid. M. J. S.

Volumetric Estimation of Metals precipitable by Alkalies, and Applications of the Method. By Dr. RUOSS (*Zeit. anal. Chem.*, 1896, 35, 143—158).—The method depends on the well-known principle that the amount of a metal precipitable by an alkali may be known from the volume of standard alkali solution (hydroxide or carbonate, according to circumstances) consumed in precipitating it from its neutral solution. Phenolphthalein is used as indicator; standard alkali is added until a slight excess is found to be present after boiling; then, without removing the precipitate, but leaving it as far as possible undisturbed at the bottom of the beaker, the excess of alkali is titrated back with standard acid. Neutral solutions may in many cases be obtained from acid ones (zinc, copper, and alumina are instanced) by evaporating with sulphuric and nitric acids to complete dryness, and dissolving the residue in water. Acid solutions may also be neutralised by an alkali with methyl-orange as indicator, but, although the author describes with great minuteness the changes which occur, with regard to which he differs from Thomson as to the point of neutrality, he seems to make little use of this method.

In estimating the alkaline earths by precipitation with sodium carbonate, a pale pink colour is obtained before the sodium carbonate is in excess, owing to the solubility of the alkaline earthy carbonate. The simplest plan is to add an excess, boil and cool, and then, with as little disturbance of the subsided precipitate as possible, add acid, drop by drop; the red colour disappears when half the excess is neutralised.

The copper in the cuprous oxide obtained in sugar estimations may

readily be estimated by the above method after dissolving in nitric acid. The presence of organic matter from a paper filter has no influence. The reduction of silver from an ammoniacal solution by glucose furnishes a new method of sugar titration, 1 mol. (179.58) of dextrose reducing 10 atoms (1076.6) of silver, so that in this case the sugar takes up twice as much oxygen as it does from cupric oxide. A silver solution containing 47.2075 grams of silver nitrate per litre will correspond with 0.005 gram of dextrose per c.c. The sugar solution is first freed from chlorides by the cautious addition of silver nitrate; milk of lime is added as usual, and the liquid diluted to 1 per cent. or less. 25 c.c. is then mixed in a flask with 50 c.c. of the silver solution, and 3 c.c. of ammonia of sp. gr. 0.875. The flask is closed with a rubber stopper carrying a long, narrow tube, and is plunged for 15 minutes into boiling water. The mixture is cooled, filtered, acidified with acetic acid, and the excess of silver estimated by standard sodium chloride (16.2518 grams per litre) taking as the result the mean between the points where silver and a chloride cease to produce turbidity in the clear filtrate.

For estimating tannin, the amount of copper precipitated from a clear, cold solution of cupric acetate (4 grams per litre) is ascertained, both before and after treatment with hide powder, adding in each case an excess of the copper solution and titrating the excess after evaporation with nitric and sulphuric acids. The tannin solution should be diluted to 0.2 per cent. or less, and nearly neutralised with either calcium carbonate or soda. The presence of gallic acid and of metallic salts does not influence the result. Using 20 c.c. of tannin solution, and 20 c.c. of copper in both experiments, and titrating with N/10 alkali, the difference between the number of c.c. of alkali consumed in the two experiments is to be multiplied by 5.1682 to obtain the result in milligrams of tannin. M. J. S.

Volumetric Estimation of Zinc. By HENRI LESCŒUR and CL. LEMAIRE (*Bull. Soc. Chim.*, 1895, [3], 13, 880—882).—In the direct titration of a soluble zinc salt with decinormal barium hydroxide, the state of dilution of the salt greatly affects the result; thus with normal or even decinormal solutions, the results are inexact; with solutions, however, of a less degree of concentration than these, exact numbers are obtained. If, however, the indirect method be employed (adding excess of barium hydroxide, and titrating back), exact results are obtained, independent of the state of dilution.

J. F. T.

Analysis of Galena. By HUGO ECKENROTH (*Chem. Centr.*, 1895, ii, 576; from *Pharm. Zeit.*, 40, 528—529).—0.5 gram of the sample is heated in a 200 c.c. flask with 25 c.c. of hydrochloric acid (sp. gr. 1.12) and 25 c.c. of water until completely decomposed, and the filtrate is then heated with small pieces of zinc until no more hydrogen sulphide is evolved. The spongy lead is dissolved in dilute nitric acid and then estimated as sulphate. L. DE K.

Analysis of Alloys of Lead, Tin, Antimony, and Arsenic. By LAUNCELOT ANDREWS (*J. Amer. Chem. Soc.*, 1895, 17, 869—873).

—Attempts to remove the tin, antimony, and arsenic by dissolving in nitro-hydrochloric acid and then repeatedly evaporating with fuming hydrochloric acid, were not successful, as the lead chloride remaining was not free from tin and antimony, but the separation was complete when the alloy was heated in a current of hydrogen chloride which had passed through strong nitric acid. Another method consists in distilling the alloy with hydrochloric acid and potassium bromide; tin and lead dissolve, and the arsenic distils, whilst the antimony should remain undissolved; the author found, however, that a little of the antimony dissolves (most likely due to the oxidising action of the air), so that he now uses potassium iodide instead of bromide. The antimony is washed through a Gooch filter with boiling water to remove lead iodide, and then dried. The author prefers converting it into sulphide by fusing it with sulphur in a current of carbonic anhydride before weighing it.

L. DE K.

Solution of Ignited Ferric Oxide and other Metallic Oxides.

By HUGO BORNTÄGER (*Zeit. anal. Chem.*, 1896, **35**, 170).—Ignited ferric oxide added to hydrochloric acid in which metallic iron (a weighed quantity of flower wire) is undergoing solution, is reduced by the nascent hydrogen, and dissolves instantly.

Many other metallic oxides behave similarly.

M. J. S.

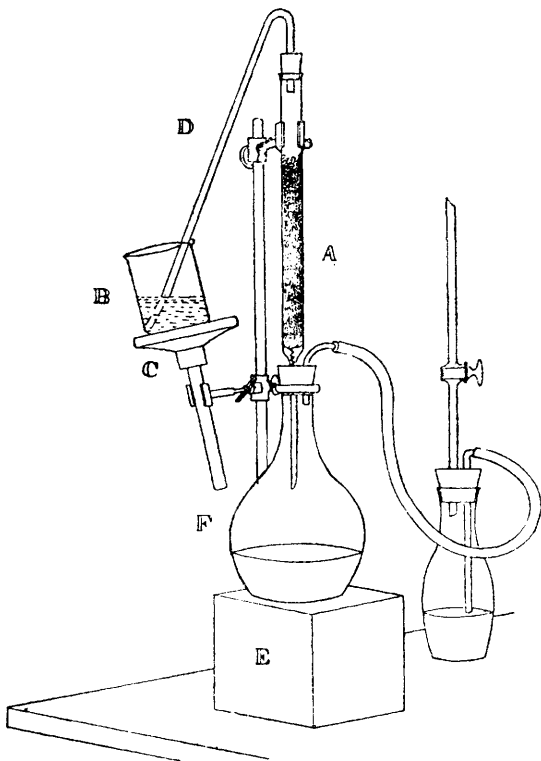
Volumetric Estimation of Titanic acid and Iron in Ores. By HORACE L. WELLS and W. L. MITCHELL (*J. Amer. Chem. Soc.*, 1895, **17**, 878—883).—Five grams of the powdered ore is heated with 100 c.c. (or more) of strong hydrochloric acid. When action ceases, 50 c.c. of dilute sulphuric acid (50 per cent. by vol.) is added, and the liquid evaporated until sulphuric acid fumes make their appearance. When cold, 200 c.c. of water is added, and, as soon as the sulphates have dissolved, the liquid is filtered into a litre flask; any insoluble matter must be fused with potassium hydrogen sulphate, and the solution of the melt added to the main liquid. The liquid is now made up to the mark, and 200 c.c. (1 gram of the sample) is reduced by hydrogen sulphide; when quite reduced, the liquid is boiled to expel the gas, and to avoid contact with air, the flask is covered with a crucible lid. After filling up to the mark with recently boiled water, the contents of the flask are rapidly cooled, transferred to a large beaker, and titrated with permanganate; the precipitated sulphur has no action on the permanganate. The titration is, of course, repeated. Another 200 c.c. is mixed in a 500 c.c. Erlenmeyer flask with 25 c.c. of sulphuric acid, and three or four rods of pure zinc suspended from a platinum wire are introduced; after boiling for 30—40 minutes, a rapid current of carbonic anhydride is passed through, and the contents rapidly cooled. The zinc is now removed, and the solution titrated with permanganate while the carbonic anhydride is still passing. The difference in the two titrations represents the titanic acid. The factor for metallic iron, divided by 0.7, is the one for titanic acid. The results are generally a trifle too low.

L. DE K.

Ammonium Phosphomolybdate and the Reducing Action of Zinc in the Reductor. By ANDREW A. BLAIR and J. EDWARD WHITFIELD (*J. Amer. Chem. Soc.*, 1895, **12**, 747—760).—The authors have prepared the yellow precipitate in 10 different ways, and investigated its composition. The water was estimated by heating the compound in a current of dry air at 250°, and absorbing the moisture in a weighed calcium chloride tube; the phosphoric acid and the molybdic acid were estimated as usual.

The following is the apparatus used as a reductor (see figure). In the bottom of the reductor tube A, is placed a spiral of platinum wire, on the top of this a piece of platinum gauze, a wad of glass wool 6 mm. thick, and then a thin film of asbestos. The tube is filled with granulated zinc to within 37 mm. of the top, and a wad of glass wool, 12 mm. thick, filling the diameter of the tube, is placed on the top. This serves to distribute the acid, and to prevent the liberated hydrogen from spattering the solution on the upper part of the tube. The solution being placed in the beaker B, the latter is put on the stand C, and the tube D placed in position. The flask F having been attached, the block E is placed under it, and, after connecting with the pump, the liquid is drawn over from B. When it is nearly all drawn over, the sides of the beaker are washed down, and it is then filled with water, and, when this is also drawn over, the stopper carrying the tube D is removed, and the reductor tube is filled with water, to thoroughly wash out the top of the tube. The flask is removed, the end of the reductor tube washed into it, the sides and neck of the flask washed down with water, and the reduced liquid titrated in the flask.

A solution of ammonium molybdate in nitric acid sooner or later



deposits a bright yellow precipitate. The authors find this to consist of 90.43 parts of molybdic acid, and 9.61 parts of water. Ammonia was only present in traces; phosphoric acid was absent.

L. DE K.

Estimation of Alcohols and Volatile acids. By EMILE DUCLAUX (*Chem. Centr.*, 1895, i, 1086; from *Ann. Inst. Pasteur*, 9, 265—280).—The process is intended for the estimation of traces of alcohol and fatty acids formed by the action of bacteria. The liquid is first neutralised, and the alcohol distilled off; its estimation will be the subject of a future paper. The remaining liquid is then acidified with tartaric acid and fractionated. To do this, 110 c.c. of the liquid is distilled, and each separate portion of 10 c.c. is allowed to run into standardised lime water; when 100 c.c. have passed over, the distillation is stopped. The first fractions contain the more volatile acids; the last fractions the less volatile ones. From the amount of lime consumed, the nature of the acid may be determined with the aid of the author's tables and curves.

L. DE K.

Estimation of Fusel Oil in refined Alcohol. By ALBERT STUTZER and R. MAUL (*Zeit. anal. Chem.*, 1896, 35, 159—162).—The method, save some small modifications, is identical with that described in *Abstr.*, 1891, 622. It is recommended that when the fusel oil does not exceed 0.1 vol. per cent., the first three-fourths of the distillate should be rejected, and the last quarter should be made up with the aqueous distillate and water to double its volume before taking its sp. gr. This should be taken with the minutest accuracy at 15°, in a pycnometer furnished with a verified thermometer (as stopper), graduated to tenths of a degree. The tables of Karl Windisch and that published in *Zeit. anal. Chem.*, 31, are recommended. The shaking apparatus seems to be the same as that previously described; it differs from that of Windisch (*Arbeit. kaiserl. Gesundheitsamte*, 5, Part II). It holds 250 c.c. of the diluted spirit and 20 c.c. of chloroform, and can be read to 0.01 c.c. Each apparatus requires to have its constant determined by an experiment with alcohol free from amylic alcohol, which is obtained by fractionating the best commercial spirit of wine, rejecting the first 20 per cent. and the last 60 per cent. The volume of the chloroform is best read at 20°, since a few degrees below this a troublesome turbidity of the alcohol is produced. With pure alcohol, the 20 c.c. of chloroform increased to 20.59 c.c.; 0.1 per cent. of amylic alcohol gave an additional increase of 0.44 c.c., and from 0.01 to 0.2 per cent. of amylic alcohol the increase in volume is proportional to the percentage.

M. J. S.

The Detection of Pentoses by Precipitation with Phloroglucinol and Hydrochloric acid. By BERNHARD TOLLENS (*Ber.*, 1896, 29, 1202—1209).—When the pentoses are warmed with hydrochloric acid and phloroglucinol, a cherry-red coloration is produced, whilst the solution exhibits a characteristic absorption band, situated on the more refrangible side of the sodium line. When the heating is continued, the solution becomes dark, and this band is obscured, a precipitate being finally formed. The author finds, however, that

when the dark-coloured precipitate is filtered off and washed, it may be dissolved in alcohol, and that the solution thus produced exhibits the absorption band quite distinctly. Thus urine containing 1 part of arabinose per thousand did not show the absorption band when placed before the spectroscope, whilst the alcoholic solution of the precipitate obtained by continued heating with the reagents named, showed it clearly. This appears to be about the limit of sensibility of the reaction, which is, however, less delicate in the presence of other sugars. The sugars themselves do not give the reaction at all; although a few of them show slight indications of a band when viewed directly. Pentoses have been detected by the use of this method in various wines, and in the sulphite liquor from the treatment of wood pulp. The urine of a sheep fed on earth-nuts and hay appeared to be quite free from pentoses.

A. H.

Estimation of Sugar by the Copper Method. By RUDOLF HEFELMANN (*Chem. Centr.*, 1895, ii, 1091—1092; from *Pharm. Centr. Halle*, **36**, 637—641).—The author recommends collecting the cuprous oxide in a Gooch's crucible, the asbestos lining of which has been freed completely from soluble matter by boiling with aqueous soda and nitro-hydrochloric acid. During the ignition, the bottom part of the crucible is closed by means of a non-perforated platinum lid. Owing to the finely divided state of the cuprous oxide, it burns rapidly and completely to cupric oxide.

L. DE K.

Estimation of Crystallisable Sugar in Raw Sugars. By FRIEDRICH STROHMER and A. STIFT (*Chem. Centr.*, 1895, i, 1010; from *Österr.-ungar. Zeit. Zucker-Ind.*, **24**, 41—74).—The authors have investigated Karcz's glycerol process (*Abstr.*, 1895, ii, 93), and describe a special apparatus for drawing off the glycerol from the undissolved sugar.

The conclusion arrived at is that, although scientifically interesting, the process is, as yet, not to be recommended for practical commercial purposes.

L. DE K.

Detection of Wood Pulp in Paper. By F. WOLESKY (*Chem. Centr.*, 1895, i, 1086; from *Österr. Ges. Chem. Ind.*, **16**, 119).—One gram of diphenylamine is dissolved in 50 c.c. of alcohol and 5—6 c.c. of strong sulphuric acid, and the sample is immersed in this solution. According to the quantity of wood pulp, a more or less decided orange colour will develop, which increases on drying.

L. DE K.

Estimation of Aldehyde in Spirits of Wine. By LUDWIG MEDICUS (*Chem. Centr.*, 1895, ii, 1060—1061; from *Forsch. Ber. Lebensm.*, **2**, 299—302).—The reagent used consists of 0.5 gram of magenta and 0.5 gram of sulphurous anhydride in 100 c.c. of water. After one to two hours, the liquid is as clear as water. The author prefers using Dubosq's colorimeter, but a couple of glass cylinders of the same diameter will answer the purpose.

The sample is first diluted until it contains from 30 to 50 per cent. of alcohol, and from 10 to 40 c.c. of the reagent is then added to 100 c.c. The mixture is now diluted with pure 30 per cent. alcohol until the colour equals that of a mixture containing a known percentage of aldehyde. The results are satisfactory. Minute traces of furfuraldehyde do not interfere.

L. DE K.

Critical Temperatures of Solutions: a New Constant for the Identification of Oils, &c. By LÉON CRISMER (*Chem. Centr.*, 1895, ii, 1059—1060; from *Chem. Rev. Fett u. Harz-Ind.*, 1895, 27, 1).—A few drops of the oil is introduced into a glass tube 9 cm. long and 5—6 mm. wide. After adding a little 90 per cent. alcohol, the tube is drawn out a few cm. above the surface of the spirit and then sealed. After being tied to a thermometer by means of platinum wire, the tube is heated in a sulphuric acid bath. The meniscus of the oil gradually disappears when the critical point is being reached. After heating another 10°, the thermometer is lifted out, and the source of heat is removed; on shaking the tube, the oil mixes completely with the alcohol; the thermometer is at once replaced in the acid, allowed to cool gradually, and the moment the mixture gets turbid, the temperature is recorded.

The author communicates the critical temperatures of some fats and ethereal oils, which prove that the process is of considerable analytical value. For instance, whilst cotton oil gives the figure 115·5, linseed oil only gives 70; butter varies from 99 to 104, and margarine and ground nut oil from 123 to 124.

L. DE K.

The Fatty Oils of *Secale cornutum* and of the Seeds of *Strophantus hispidus* and *Hyoscyamus niger*. By J. ALFRED MJÖEN (*Arch. Pharm.*, 234, 278—283, 283—286, 286—289).—The following are some of the analytical results obtained with these oils.

	<i>Secale cornutum.</i>	<i>Strophantus hispidus.</i>	<i>Hyoscyamus niger.</i>
Specific gravity at 15°.....	0·9254	0·9285	0·939
Saponification number.....	178·4	187·9	170·4
Iodine number.....	71·08	73·02	138·0
Acetyl number.....	62·9	0·0	0·0
Melting point of fatty acids.....	39·5—42°	28—30°	—

The oil from *Secale cornutum* contains cholesterol and the glycerides of palmitic and oleic acids, together with that of a hydroxy-acid which has not been isolated. The two other oils consist mainly of the glycerides of oleic and palmitic acids, that of *Hyoscyamus niger* also containing the glyceride of another unsaturated acid.

A. H.

Iodine Number and Refractive Index of Cacao Butter. By A. STROHL (*Zeit. anal. Chem.*, 1896, 35, 166—169).—The very wide limits 32—51 have been found by different investigators. The

author, having special facilities for obtaining theobroma kernels from almost all the known sources, has himself extracted the fat from upwards of 40 specimens, and has obtained results varying from 32.8 to 41.7. The refractive indices of the same samples ranged from 1.4565 to 1.4578 at 40°, and showed a certain degree of parallelism with the iodine numbers. M. J. S.

Estimation of Benzidine and Tolidine. By WILHELM VAUBEL (*Zeit. anal. Chem.*, 1896, **35**, 163—164).—Benzidine and tolidine are best estimated by titration with a nitrite. In the commercial substances they are, however, accompanied by other bases which also consume nitrite, but which, in the manufacture of congo dyes, do not yield direct cotton dye-stuffs, although they influence the purity of the colours produced. It is therefore necessary to precipitate the benzidine or tolidine from the hydrochloric acid solution by the addition of sulphuric acid or a sulphate, and to titrate the unprecipitated bases. A correction may be made for the solubility of the sulphates.

	Benzidine.	Tolidine.
1 litre of water dissolves.....	0.0076 gram.	0.03 gram.
1 litre of water + 20 c.c. of 35 per cent. hydrochloric acid, dissolves.....	0.02 „	0.513 „
1 litre of water + 50 c.c. of 35 per cent. hydrochloric acid, dissolves.....	0.48 „	4.42 grams.

Estimations made as above showed 0.2—0.55 per cent. of foreign bases in benzidine, 2.8—5 per cent. in tolidine.

The melting point should not be below 125° for benzidine, or 120° for tolidine (see also Abstr., 1895, ii, 489). M. J. S.

Behaviour of Naphthols and Naphthylamines with Nascent Bromine. By WILHELM VAUBEL (*Zeit. anal. Chem.*, 1896, **35**, 164—166).—This continuation of the author's work (Abstr., 1895, i, 55; 1894, i, 19, 453) has been undertaken with the object of developing analytical methods for the above compounds. The substance was in each case dissolved in glacial acetic acid and treated with a mixture of potassium bromide and bromate with addition of hydrochloric acid.

α -Naphthol rapidly takes up two atoms of bromine, and then further absorption continues more slowly. No sharp end to the reaction can be observed.

α -Naphthol ethyl ether, β -naphthol, β -naphthol methyl ether, and β -naphthol ethyl ether each take up one atom of bromine with sharp end to the reaction, so that the method can be used for their estimation.

Acet- α -naphthylamide and aceto- β -naphthylamide each take up one atom with a termination sharp enough to be recognised, but on adding more of the reagent further bromination slowly takes place.

β -Naphthylamine takes up rapidly more than two atoms, but with no sharp end to the reaction.

α -Naphthylamine behaves somewhat similarly.

M. J. S.

The Behaviour of Narcotine and Papaverine in the Stas-Otto Method of detecting the Alkaloids. By ROBERT OTTO (*Arch. Pharm.*, 1896, **234**, 317—320).—The statement that papaverine is extracted by ether from its solution in aqueous tartaric acid (*Anleitung zur Ausmittlung der Gifte, &c., 6te. Auflage*, 252) was founded on experiments with a sample of so-called papaverine which really consisted mainly of narcotine. The latter is slowly extracted by ether from such a solution, readily from an alkaline solution, whilst papaverine is only extracted in exceedingly small amount from a tartaric acid solution, and not very readily from an alkaline solution. A. H.

Detection of Fatty Oils in Copaiba Balsam: a new Test for Gurjun Balsam. Detection of Colophony in Guaiacum Resin and Balsams of Tolu and Copaiba. By EDUARD HIRSCHSOHN (*Chem. Centr.*, 1895, ii, 694; from *Pharm. Zeit. Russ.*, **34**, 497—499; 499—501; 513—515; 515—517).—The presence of fatty oils in copaiba may be detected by boiling 20—40 drops of the sample with 1—2 c.c. of a solution of 1 part of sodium hydroxide in 5 parts of 95 per cent. alcohol; the solution should not gelatinise on cooling, nor even on adding twice its volume of ether. The sample should also dissolve completely in 3 vols. of 90 per cent. alcohol, and not deposit any oily drops after being at rest for an hour.

To test for gurjun balsam, the sample of copaiba is boiled with 3 vols. of 95 per cent. alcohol and 1 part of crystallised stannous chloride. If the sample is adulterated, it will first turn reddish, and finally blue.

To test guaiacum resin and balsam of tolu for added colophony, the sample is agitated with 4—5 times its bulk of light petroleum, and the filtrate is shaken with its own volume of copper acetate solution (1—1000), when no green colour should be seen in the petroleum layer. To detect the presence of colophony in balsam of copaiba, it has been recommended to triturate the sample with 5 parts of solution of ammonia, and notice whether any gelatinisation takes place. The author, however, finds this test to be untrustworthy.

L. DE K.

Estimation of Jalap Resin in Medicines. Detection of Strychnine in Corpses. By EDUARD SPAETH (*Chem. Centr.*, 1895, ii, 625; from *Forsch. Ber. Lebensm.*, **2**, 224—226).—The medicine containing sugar is mixed with water and whirled in a Soxhlet's centrifugal apparatus. The separated jalap resin is collected, washed with water, dissolved in alcohol, and, after evaporating the latter, the residue is dried over sulphuric acid and weighed. Pills are first extracted with alcohol, the liquid diluted with water, and then treated as above.

The author confirms the statement that strychnine can be satisfactorily detected in corpses which have been buried from two to six months.

L. DE K.

General and Physical Chemistry.

Optical Rotatory Power of Substances in the Crystalline and Liquid States. By HERMANN TRAUBE (*Sitzungsber. Berl. Akad.*, 1895, 10, 195—205).—The author has determined the specific rotations of a number of uniaxial crystalline substances which are circularly polarising, both in the crystalline and the melted or dissolved states.

The hexagonal trapezohedral tetartohedral crystals of patchouli camphor have a rotation for the D line of -1.325° per mm. in the optic axial direction. In the fused state, the camphor has the specific rotation $[\alpha]_D = -118^\circ$, and in alcoholic solution, of $[\alpha]_D = -124.5^\circ$ (Montgolfier, this Journal, 1877, i, 478); these numbers correspond with rotations of -1.240° and -1.308° per mm. respectively of the amorphous substance. It is thus obvious that patchouli camphor has practically the same specific rotation, both in the crystalline and amorphous states. The same is true of ordinary camphor, which crystallises in the same sub-system.

Matico-camphor also crystallises in the hexagonal trapezohedral tetartohedral system, the crystals having a sp. gr. of 1.080 at 15° and a rotation of -1.877° for the D line in plates 1 mm. thick. The melted substance has the specific rotation $[\alpha]_D = -29.17^\circ$, from whence it can be calculated that the rotatory power is about six times as great in the crystalline as in the melted state.

Rubidium tartrate separates from aqueous solution in anhydrous, hexagonal, trapezohedral crystals, having the sp. gr. 2.694 at 14° ; $a : c = 1 : 1.82396$; the crystals of the dextrotartrate are lævoptatory, whilst those of the lævotartrate are dextro-rotatory. Plates 1 mm. thick have the rotation of 10.12 to 10.24° for the D line; the rotation in aqueous solution, referred to a thickness of 1 mm., is 0.69° , and of the opposite sign to that of the crystals. The author points out that there is nothing unusual in the great differences, both in sign and magnitude of the rotation in the two states, as the sign and magnitude of the specific rotation of a substance depend so much on the solvent. Rubidium racemate crystallises with $2H_2O$ in large monosymmetric plates at low temperatures, but at higher ones is deposited as a mixture of the constituent tartrates. Rubidium and potassium tartrates will not crystallise together as an isomorphous mixture.

Cæsium dextrotartrate is isomorphous with the rubidium salt, $a : c = 1 : 1.80754$; the crystals have the sp. gr. 3.03 at 14° , and a rotation of -14° to -19° per mm. for the D line. The rotation of the crystals is thus of opposite sense to that of the aqueous solution.

W. J. P.

The Dielectric Constant of Liquid Mixtures. By CHARLES E. LINEBARGER, (*Zeits. physikal. Chem.*, 1896, 20, 131—134).—The dielectric constants were determined in the case of various mixtures of the following:—Benzene | ether; benzene | ethylic acetate; benzene | carbon tetrachloride; toluene | ethylic benzoate; toluene | turpentine; toluene | carbon bisulphide; chloroform | carbon tetrachloride; carbon

bisulphide | carbon tetrachloride; carbon bisulphide | chloroform; carbon bisulphide | ether. In no case can the constant be accurately calculated by the simple mixture rule, the actual numbers being lower than the calculated in all cases except in those mixtures where ether was one of the components, when the reverse obtained. The dielectric constants were determined by the method described by Nernst (Abstr., 1894, ii, 437).
L. M. J.

Electrolysis of Water. By ALEXEI P. SOKOLOFF (*Ann. Phys. Chem.*, 1896, [2], **58**, 209—248).—According to Helmholtz, the E.M.F. required for the electrolysis of water depends directly on the densities of the hydrogen and oxygen at the electrodes; the smaller these densities the weaker will be the E.M.F. required, and in a liquid from which all gas has been completely removed, the value must sink to zero. Helmholtz has further deduced an expression connecting the E.M.F. of polarisation, A , for any pressures, p_h and p_o , of the hydrogen and oxygen, with the E.M.F. when the pressure p_a is the atmospheric, and determined the value of this last quantity, A_a , as being 1.783 volts. A direct proof that the decomposition of water can be accomplished with any E.M.F., however small, has not yet been given, nor can Helmholtz's determination of A_a be regarded as final; the author has therefore submitted these points to further experimental investigation.

In order to obtain proof of electrolysis when the E.M.F. is very small, a voltameter was arranged, which contained two platinum plates as electrodes, and in the immediate neighbourhood of each plate an insulated platinum point. When a current is passed, the electrodes become polarised by gas layers of definite density, but as these gases are electrically neutral, and therefore quite free, they diffuse through the liquid, and must, in a short time, reach the platinum points and polarise these just as each electrode was originally polarised. This polarisation can then be easily detected by means of a sensitive electrometer. The experiments quoted in the paper, in which this arrangement was employed, show that electrolysis can be produced by any E.M.F. however small.

In contradiction to Helmholtz, the author finds that an E.M.F. of 1 volt suffices to produce gas of measurable pressure by the decomposition of water. Thus, in one experiment, which lasted 16 months, a calomel cell (1.072 volt) produced gas of 2.53 mm. pressure, and from the continual increase in the pressure, this seems to be even far below the limiting value. From the results it appears that difficulties are encountered in producing invisible electrolysis with a small E.M.F., similar to those met with when visible electrolysis is effected. Forces are active on the surfaces of the electrodes which restrain the gases from freely diffusing through the liquid, and bring about absorption of the gases by platinum and other metals.

The forces here spoken of introduce difficulties in the determination of A_a from the results of experiments on visible electrolysis. Determinations which the author has made at low pressures give a value for A_a of 0.745 volt, which is much smaller than that given by Helmholtz.
H. C.

New Electrolytic Apparatus. By DONATO TOMMASI (*Compt. rend.*, 1896, **122**, 1122—1123).—The anode consists of a pair of metallic plates or perforated cylinders containing granular metal, &c., whilst the cathode is a metallic disc which revolves between them. Only a segment of this disc is immersed in the liquid, and that part which is above the liquid passes between brushes, which remove both the spongy deposited metal and the bubbles of gas. The metal thus rubbed off is collected in a special form of receiver. By this arrangement, not only is polarisation entirely prevented, but the deposited metal is removed out of danger of subsequent attack by the electrolyte. The resistance of the electrolytic cell is also considerably reduced, because the cathode can be placed very close to the anode, and the agitation caused by the rotating disc maintains uniformity of composition throughout the whole volume of the electrolyte.

C. H. B.

Electrolytic Dissociation in Solvents other than Water. By GIACOMO CARRARA (*Gazzetta*, 1896, **26**, i, 119—195; compare Abstr.,

Substance.	Methylic alcohol.		Water.	
	μ_{∞} .	$\mu_{1024} - \mu_{32}$.	μ_{∞} .	$\mu_{1024} - \mu_{32}$.
HCl	133.08	—	395.2	—
HI	134.5	—	397.0	—
LiCl	77.30	18.58	110.0	11.5
KOH	75.75	6.00 ?	237.6	—
KOMe	77.8	—	—	—
KCl	95.57	22.46	140.8	12.6
KBr	96.52	19.72	143.6	12.6
KI	97.63	18.85	142.6	12.2
NaOH	71.83	—	216.2	—
NaOMe	74.5	—	—	—
NaCl	86.80	20.01	119.4	11.9
NaBr	87.57	19.62	122.2	12.0
NaI	89.77	15.78	121.4	15.7
NH ₄ OH	82.0	—	237.4	30.72
NH ₄ Cl	96.24	24.78	140.6	—
NH ₄ Br	99.93	22.32	143.4	—
NH ₄ I	105.25	20.57	142.6	—
NH ₄ F	97.6	31.07	121.2	—
NEt ₄ OH	91.13	—	199.2	—
NEt ₄ Cl	95.76	20.77	102.4	—
NEt ₄ Br	96.62	20.01	105.2	11.3
NEt ₄ I	113.76	34.01	104.2	—
NMe ₄ I	115.3	39.0	115.6	—
SMe ₃ OH	97.34	—	214.0	—
SMe ₃ Cl	100.09	27.6	117.8	—
SMe ₃ Br	102.5	28.9	120.3	—
SMe ₃ I	116.38	36.65	119.3	—
SEt ₃ I	112.53	—	107.6	—
CH ₃ COONa	70.32	20.92	87.6	10.5
CCl ₃ COOH	121.48	—	358.0	—
CCl ₃ COONa	73.98	18.96	82.0	9.6

1895, ii, 302).—The author has determined the electrical conductivities of a large number of inorganic and organic salts in methylic alcohol solution. The values of the electrical conductivity at infinite dilution, μ_{∞} , and the differences of the conductivities for the volumes 1024 and 32, $\mu_{1024} - \mu_{32}$, both for methylic alcohol and aqueous solutions, are given in the appended table. The determinations show that methylic alcohol exerts a dissociating effect on most electrolytes comparable to that exerted by water, and the mode of change of the molecular conductivity in the alcoholic solution is quite analogous to that occurring in aqueous solution; it therefore seems justifiable to apply the methods of calculating ionic velocities and limiting values of the molecular conductivity, μ_{∞} , used for aqueous solutions, to solutions in methylic alcohol. No constant ratio exists between the conductivities of solutions of electrolytes in water and methylic alcohol; usually the limiting values are smaller in the latter solutions, but sometimes they are equal to, or even greater than, the molecular conductivities in aqueous solution. In some cases, especially those of tetrethylammonium and trimethylsulphinic hydroxides and iodides, the values of μ_{∞} in the alcoholic solution do not seem to be merely the sums of constant ionic velocities; if the calculated values of μ_{∞} are trustworthy, it consequently follows that the velocity of migration of an ion can depend on the other ion present in solution; quite possibly, however, these calculated values do not correspond to wholly dissociated salts, but only to some definite states of equilibrium at equal concentrations. For the same substance, the degree of dissociation calculated from the rise in boiling point of the solvent, and from the conductivity determinations, are not identical. The law of dilution holding in aqueous solution, seems also to apply in general to solutions in methylic alcohol; Ostwald's formula gives better results for acids and bases, whilst that of Rudolphi answers better for salt solutions. The order of magnitude of the conductivities of the various electrolytes is not the same in aqueous as in methylic alcohol solution.

W. J. P.

Variations of Electrolytic Dissociation with Temperature: Freezing and Boiling Point Determinations of Aqueous and Methylic Alcohol Solutions of Chlorides. By ROBERTO SALVADORI (*Gazzetta*, 1896, 26, i, 237—254).—The aqueous solutions of many chlorides, such as those of cobalt, nickel, manganese, and copper, change colour as the temperature rises just as they do when concentrated; this fact is usually explained by assuming that heating causes a decrease in electrolytic dissociation just as does an increase in concentration, so that if one or both of the ions differ in colour from the non-dissociated chloride, the colour of the solution changes. The author demonstrates the decrease in dissociation attending rise in temperature by cryoscopic and ebullioscopic determinations with aqueous solutions of the above chlorides; the degree of dissociation found by the cryoscopic method is always greater than that shown at the higher temperature by the boiling point method.

The degree of dissociation calculated from the rise in boiling point of methylic alcohol solutions of the chlorides is much less than in

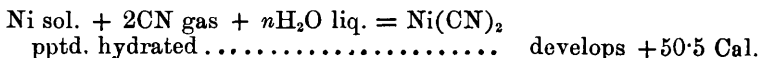
aqueous solutions; this is especially the case with cobalt chloride, which, judging by the colour of the alcoholic solution, should be much more highly dissociated. Mercuric chloride is more highly dissociated in methylic alcohol than in water; Beckmann (*Abstr.*, 1891, 389) has shown that this chloride is dissociated to a less extent by ethylic alcohol than by water.

W. J. P.

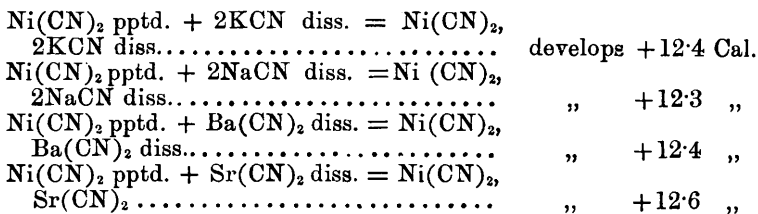
Thermo-elements of Amalgams and Electrolytes. By AUGUST HAGENBACH (*Ann. Phys. Chem.*, 1896, [2], 58, 21—36).—The author determined the thermo-electromotive force for elements consisting of the following chain: Cadmium amalgam | solution of a cadmium salt | cadmium amalgam, and of a similar chain for lead. The sulphate, nitrate, chloride, bromide, and iodide of cadmium, and the nitrate and chloride of lead were employed at various concentrations. One electrode was maintained at a temperature of about 6°, and readings taken with the second electrode at temperatures ranging from 6° to 80°. The thermo-electromotive force was found to be approximately proportional to the temperature, except for lead chloride, where it remained almost constant from 30° to 50°, whilst, contrary to expectation, the E.M.F. decreases with increasing dilution, the decrease varying with the different salts.

L. M. J.

Thermochemistry of Nickel Cyanide. By RAOUL VARET (*Compt. rend.*, 1896, 122, 1123—1125).—The heat of formation of nickel cyanide was measured by precipitating nickel sulphate solution with potassium cyanide and sodium cyanide solutions, and also by treating nickel nitrate solution in a similar manner. The different determinations agree closely, and the mean result is



Measurements of the heat of dissolution of nickel cyanide in solutions of cyanides of the alkalis or alkaline earths gave the following results.



These results show that the soluble so-called double cyanides (which are not dissociated by dialysis) may be regarded as derived from a complex nickelocyanic acid, which, however, seems not to exist in the free state.

C. H. B.

Adiabatic Volume Changes in Solutions. By K. ROGÓYSKI and GUSTAV TAMMANN (*Zeits. physikal. Chem.*, 1896, 20, 1—18).—By the application of the gaseous expression connecting the coefficient

of expansion, specific heat, and temperature change for adiabatic compression, to the case of liquids where the external work is negligible, the equation $d_Q T/dp = T/C_p \cdot d_p v/dT$ is obtained, which, by integration and the expression of C_p in calories, yields

$$\Delta_Q T = \int_{p_1}^{p_2} T/Ec_p \cdot dv/dT \cdot dp.$$

Necessary data for dv/dT and C_p as functions of p are obtained from Amagat's numbers, and the values of $\Delta_Q T$ are calculated for pressures from 100 to 2,000 atmospheres at 0° , formulæ for other temperatures being also given, the results agreeing fairly well with existing data. By the substitution of $p + \Delta\kappa$ for p , the equation is applicable to solutions, $\Delta\kappa$ being the internal pressure of the solution. By measurements of the resistance and use of the known temperature coefficients, the temperature changes for the release of compression are determined for solutions of potassium chloride, sodium chloride, zinc sulphate, sulphuric acid, and sodium chloride in dilute ethylic alcohol. The results are compared with those theoretically calculated, and show throughout a very satisfactory agreement, although, in the authors' opinion, the differences are greater than the experimental errors (see also this vol., ii, 289; Abstr., 1895, ii, 307, and previous abstracts). L. M. J.

Dissociation of Halogen Salts. By ALEXANDR A. JAKOWKIN (*Zeits. physikal. Chem.*, 1896, 20, 19—39).—In the author's previous communication on the dissociation of potassium triiodide (Abstr., 1894, ii, 271), the value of the constant was determined, assuming the partition ratio between carbon bisulphide and water to be 410/1, whereas the author has since determined this ratio to be 680—585 (this vol., ii, 295). The previous results are, therefore, recalculated, the dissociation constant being found to vary only very slightly; to be greater for potassium tribromide than for the triiodide, and greater for the potassium than for the hydrogen salts. As I_3 exists as an independent ion, the dissociation in dilute solutions should be independent of the metallic ion, a conclusion verified in the case of lithium, sodium, potassium, and barium iodides. As the coefficient of absorption is altered by the solution of other salts, the partition ratios of bromine, and iodine in carbon tetrachloride, and carbon bisulphide, and various salt solutions were determined, and in these cases Setchenoff's absorption law is found to hold good. The dissociation of various mixed halogen salts in water and salt solutions were also examined. In the case of the bromide, the results indicate the probability of the formation of higher halogen compounds, such as KBr_3 , at higher concentrations. L. M. J.

Freezing of Dilute Solutions. By I. ZOPPELLARI (*Gazzetta*, 1896, 26, i, 116—118).—The fact that on cooling a dilute solution, the pure solvent solidifies first, whilst the dissolved substance becomes concentrated in the residual solution, may be well demonstrated by cooling a 0.03 per cent. aqueous solution of potassium permanganate contained in a small beaker at -5° ; after some hours

the beaker is found to be lined with colourless ice, whilst the deeply coloured liquid core of the mass retains all the permanganate in solution.

W. J. P.

Cryoscopic Behaviour and Composition of some Acetates of Feeble Bases. By I. ZOPPELLARI (*Gazzetta*, 1896, 26, i, 255—264; compare Ghira, *Abstr.*, 1893, i, 667; 1894, i, 226).—The author has analysed and examined the cryoscopic behaviour in benzene solution of the acetates of piperidine, diisoamylamine, diisobutylamine, coniine, dipropylamine, and phenylhydrazine; these salts all consist of one molecule of base to one of acid with the exception of the last, which contains two molecules of acid. Picoline acetate depresses the freezing point of benzene normally, but the ethylaniline salt gives a very large molecular depression, just as Ghira found with the acetates of aniline and diethylaniline; dipropylamine acetate gives a very low molecular depression, whilst phenylhydrazine acetate gives the normal depression in a 3 per cent. solution, and a very large molecular depression in a 0.6 per cent. solution. The high molecular depressions found with the acetates of aniline and its alkyl derivatives are the sums of those due to the base and to the acid, showing that the salts are dissociated in benzene; the very low molecular depressions obtained with the acetates of diethylamine, coniine, dipropylamine, diisoamylamine, and piperidine may be due either to doubling of the molecule, or to the formation of acid acetates in benzene solutions. A comparison of the molecular depressions of the freezing point of benzene by these salts with the affinity constants K of the bases reveals an intimate connection; the molecular depression decreases regularly as the affinity constant becomes greater.

W. J. P.

Reaction Velocity in the Conversion of Diazoamido- into Amidoazo-derivatives. By HEINRICH GOLDSCHMIDT and R. U. REINDERS (*Ber.*, 1896, 29, 1369—1377).—The object of this investigation was to determine the influence of temperature, solvent, and quantity of reacting substances on the reaction velocity in the conversion of diazoamido- into amidoazo-compounds; light might also be thrown on the part played by the catalytic agent. The present communication is confined to the investigation of the action of aniline hydrochloride on diazoamidobenzene in aniline solution; the statement frequently made that the hydrogen chloride converts the diazoamidobenzene into diazobenzene chloride and aniline, and that these then combine, forming amidoazobenzene, is incorrect, since solid diazobenzene chloride and aniline or paratoluidine first yield diazoamido-derivatives, which are only slowly converted into amidoazo-compounds.

The aniline (25 or 50 grams) was weighed into corked flasks, the necessary quantity of aniline hydrochloride dissolved in it, and the flasks heated in a water bath of constant temperature; diazoamidobenzene was then added, and, after the requisite time had elapsed, a portion of the mixture was withdrawn and the reaction arrested by the addition of soda. The analysis of the product is based on the

fact that diazoamidobenzene, when heated with dilute acid, evolves two-thirds of its total nitrogen, whilst amidoazobenzene is not changed under these conditions. The nitrogen was evolved and collected in an apparatus designed by the authors, and which is fully described. Hempel's burette was not found to be convenient. The velocity constant, K , was calculated from the formula $K = \frac{l}{t} \log \frac{a}{a-x}$, where t = the time in hours.

Influence of the Concentration of the Aniline Hydrochloride Solution on the Velocity Constant.—Aniline hydrochloride, 0.1, 0.2, 0.3 parts in 1,000 of aniline, $K = 0.0060, 0.0123, 0.0181$ respectively, whence it follows that, as in many monomolecular reactions, K is proportional to the concentration of the catalytic agent.

Influence of Temperature.—The value of K at $25^\circ, 35^\circ, 45^\circ$, and $55^\circ = 0.0060, 0.0246, 0.0810$, and 0.2530 respectively, the values calculated by means of van't Hoff's expression, $\log K = -\frac{A}{T} + B$, using the known values at 25° and 45° , are 0.0231 and 0.2640 for 35° and 55° respectively.

Concentration of the Diazoamidobenzene.—As normal solution, one containing in 1000 grams aniline, 0.5 gram-molecule of diazoamidobenzene, was employed; the temperatures selected were 35° and 55° , for $N\frac{1}{2}$ solutions, $K_{0.1} = 0.0246$ and 0.2530 respectively; for $N\frac{3}{4}$ solutions the values are 0.0250 and 0.2640 respectively. For solutions of moderate strength, the concentration of the diazoamidobenzene is practically without influence on the velocity of the reaction. The directions, found by practice to give the best yield of amidoazobenzene, and given by E. Fischer in his "Organischer Präparate," are almost identical with the conditions which calculation from the above values indicates as the most favourable. J. B. T.

A new form of Mercury Air-pump. By R. W. WOOD (*Ann. Phys. Chem.*, 1896, [2], 58, 205—208).—The author describes a form of mercurial pump intended chiefly for the production of Röntgen vacuum tubes. Diagrams of the instrument, with the method of use, are given. L. M. J.

Automatic Apparatus for Filtration at High Temperatures. By J. J. POSTOLÉFF (*Chem. Centr.*, 1895, ii, 1—2; from *Wratsch*, 1895, 182).—The apparatus consists of a hot water funnel of the usual construction. The steam escaping from the jacket is conducted, by means of a rubber tube, to a flask which, together with the burner used for heating, is fixed on a revolving lever attached to the base of the tripod which carries the funnel. The lever is kept in position by a counterpoise, but when a given quantity of water has condensed in the flask, the lever turns, and thus removes the burner from below the heating jacket. As the funnel cools, it draws the water back out of the flask, the lever turns, and brings the burner into position again. In cooling, the temperature falls $2-3^\circ$, and the apparatus can be left to itself for 24 hours. J. J. S.

Inorganic Chemistry.

Electrolytic Formation of Hypochlorites and of Chlorates.

By FELIX OETTEL (*Chem. Centr.*, 1895, i, 592—593; from *Zeits. Elektrotechn. u. Elektrochemie*, 1895, 354—361, and 474—480).—The electrolysis of potassium chloride solutions was studied with the following apparatus. The current was obtained from four accumulators; in the circuit were arranged a copper voltameter for measuring the current, a voltameter for collecting the electrolytic gas, the cells in which the experiments were carried out, an ampère meter, and a resistance box. The gas voltameter was filled with caustic soda solution, and was provided with electrodes consisting of two concentric cylinders of nickel foil. The cell in which the actual experiments were performed had a capacity of about 115 c.c., and was closed by a sheet of rubber closely screwed down; through the rubber passed the electrodes (platinum foil and wire), a capillary delivery tube, and an ordinary glass tube reaching to the bottom of the cell and serving to empty or fill it. A current of 1—1.2 ampère was used, and was allowed to run for two hours. When neutral solutions are electrolysed, the main product is hypochlorite. At the end of the experiment 83 per cent. of the active chlorine exists as hypochlorite and 17 per cent. as chlorate. The addition of an alkali favours the decomposition of the water, and decreases the amount of hypochlorite formed, but increases the amount of chlorate. Raising the temperature has pretty much the same influence as the addition of alkali.

A less dense current at the cathode favours the reduction of hypochlorite, and has the greatest effect in a concentrated solution, either neutral or slightly alkaline; a diminution in the density of the current at the anode increases the amount of water decomposed; the difference is less marked in a strongly alkaline solution.

In an alkaline solution, the reduction is reduced to a minimum, and hence it is not necessary to use a diaphragm (membrane).

Sodium chlorate can be obtained in a similar manner; sodium hydroxide increases the amount of chlorate formed, even more than potassium hydroxide. J. J. S.

Manufacture of Potassium Chlorate. By K. J. BAYER (*Chem. Zeit.*, 1895, 19, 1453—1455).—The author describes a new method for the manufacture of potassium chlorate. Chlorine is lead into a cream of zinc oxide and water; zinc oxychloride and hypochlorite are first formed, but, finally, a clear solution of zinc chloride and hypochlorite is obtained. The conversion of the hypochlorite into chlorate readily takes place when this solution is heated with the requisite quantity of potassium chloride, and the yield is almost theoretical. A still better method is to add the requisite quantity of potassium chloride to the zinc oxide and water before the chlorine is passed in, and then to keep the temperature at about 90—95° during the

chlorination. The resulting solution may be evaporated down to 30° Bé., when, on cooling, the greater part of the potassium chlorate crystallises out in nearly pure form. A further quantity may be obtained by concentrating the mother liquors to 60° Bé.

The final mother liquor is treated with hydrochloric acid, and then evaporated down till the zinc chloride solidifies. The mode of working and the appliances used are almost identical with those employed in the manufacture of potassium chlorate by the lime method.

J. J. S.

The Density of Oxygen. By EDWARD W. MORLEY (*Zeits. physikal. Chem.*, 1896, **20**, 68—130).—Three series of determinations were made. In the first of these all necessary corrections were applied; in the second corrections for the expansion of the glass and thermometric corrections were eliminated as the gas was brought into pressure and temperature equilibrium with a similar flask containing the normal volume of hydrogen; whilst in the third series the temperature was throughout the experiment that of melting ice. The capacity of the flasks, internal, and external, were determined by (1) weight in air, (2) additional weight to maintain equilibrium, when the flask was immersed in water; (3) loss of weight when filled with water and weighed in water of equal temperature. The oxygen employed was prepared from potassium chlorate, and also in the third series by electrolysis, and every precaution observed to ensure purity. The author estimates the quantity of nitrogen present to be not more than 1/30,000, and of chlorine not more than $\frac{1}{30}$ milligram in 20 litres, whilst the carbonic anhydride, and mercury vapour are also quite negligible. The details of the apparatus used, of the filling and evacuation of the flasks, &c., and the experimental numbers are given in the paper. The agreement of the several experiments indicate the very great care with which the determinations were made, the final results being

- (1). $D = 1.42879 \pm 0.000034$ (mean of 9).
- (2). $D = 1.42887 \pm 0.000048$ (mean of 15).
- (3). $D = 1.42917 \pm 0.000048$ (mean of 24).

The author considers that of these the third should receive double weight, and hence obtains as a mean of the whole series $D = 1.42900 \pm 0.000034$ (Abstr., 1895, ii, 261).

L. M. J.

Tubular Ozone Generator. By GASTON SEGUY (*Compt. rend.*, 1896, **122**, 1120—1121).—Each generator consists of a glass tube containing seven narrow tubes, each of which has a spiral of aluminum wire inside and outside. The inside spirals are all connected with a single wire which passes to the outside of the large tube, whilst the external spirals are similarly connected with another wire. These wires are respectively connected with the two poles of an induction coil. Three or more of the generators may be connected in series, and 170 milligrams of ozone per hour can be obtained from air, and 250 milligrams per hour from oxygen.

C. H. B.

Formation of Persulphuric acid. By KARL ELBS and O. SCHÖNHERR (*Chem. Centr.*, 1895, i, 591—592; from *Zeits. Elektrotechn. u. Electrochemie*, 1895, 417—420 and 468—472).—The authors have determined the relationship between the amount of persulphuric acid formed, and the concentration of the sulphuric acid which is electrolysed. The persulphuric acid was estimated by pouring 5—10 c.c. of the liquid into 200—300 c.c. cold water, adding a given quantity of ferrous ammonium sulphate and titrating back with potassium permanganate. If the density of the sulphuric acid is below 1.2, very little persulphuric acid is formed; the maximum amount is obtained when the acid has a sp. gr. = 1.35—1.5. The persulphuric acid is formed by the union of HSO_4 ions at the anodes, and is not due to oxidation, since the amount formed is greater with a stronger current, whereas if it were a simple oxidation product the amount formed would decrease with an increase in the strength of the current. Too great a concentration of the acid retards the formation of persulphuric acid for several reasons:—(1) Concentrated acid is a bad conductor; (2) the molecules of $\text{H}_2\text{S}_2\text{O}_8$ when formed in a concentrated acid are not so free to move as in the more mobile dilute acid, and hence remain a longer time at the anode and become decomposed; (3) with concentrated acid, the amount of heat developed is greater and hence destroys a greater number of persulphuric acid molecules.

When a strong current is passed through a moderately dilute acid, it is broken. On warming, however, the electrolysis begins anew. This stoppage is caused by the accumulation of too many ions, and the formation of a coating of the non-conducting $\text{H}_2\text{S}_2\text{O}_8$ molecules round the anode.

The amount of persulphuric acid formed is also diminished by increase of temperature; at 60° it is decomposed as rapidly as formed. With dilute acid (sp. gr. < 1.3) practically no hydrogen peroxide is formed by the decomposition of the persulphuric acid, the amount of peroxide, however, increases with the strength of acid.

When diluted with 50 times its volume of cold water, persulphuric acid is not decomposed. J. J. S.

Persulphuric acid. By KARL ELBS (*Chem. Centr.*, 1895, ii, 476—477; from *Zeits. Elektrotechn. u. Electrochemie*, 1895, 162—163).—In order to demonstrate the formation of persulphuric acid and of its potassium salt, a wide test tube is filled with the electrolyte, the anode being a platinum wire enclosed for the greater part of its length in a glass tube, and the cathode a platinum ring. A wider tube, surrounding the anode, collects the bubbles of gas evolved and prevents their reaching the cathode. The whole apparatus is placed in a beaker of cold water. A current of 100 amperes per square metre anode surface is used. With sulphuric acid of sp. gr. 1.4, persulphuric acid can be detected in the liquid round the anode after five minutes. With a cold saturated solution of potassium sulphate in dilute sulphuric acid, a considerable amount of crystallised potassium persulphate is obtained at the end of 10 minutes. The ammonium salt requires a longer time. The same apparatus may be used for

showing the conversion of cobaltous into cobaltic salts. The author also proves that Darrieus and Schoops' hypothesis of lead accumulators (compare *Chem. Centr.*, 1895, i, 522) is not tenable; since lead dioxide is only formed by persulphuric acid in nearly alkaline solutions. J. J. S.

Position of Tellurium in the Periodic System. By JAN W. RETGERS (*Zeits. anorg. Chem.*, 1896, 12, 98—117).—A controversial paper dealing with the results published by Staudenmaier (this vol., ii, 96). E. C. R.

Hyponitrous acid. By ARTHUR R. HANTZSCH (*Ber.*, 1896, 29, 1394).—The author in conjunction with Ludwig Kaufmann, has prepared hyponitrous acid in the solid form, together with an ethereal salt and the ammonium salt. Further details will shortly be published. (Compare Tanatar, this vol., ii, 417.) A. H.

Action of Hydrogen Bromide on Thiophosphoryl Chloride. By ADOLPHE BESSON (*Compt. rend.*, 1896, 122, 1057—1060).—Carefully purified thiophosphoryl chloride melts at -35° . It is not attacked at its boiling point by hydrogen bromide, but if the gas mixed with vapour of the thiophosphoryl chloride is passed over pumice heated at $400-500^{\circ}$, decomposition takes place, and the product contains the three derivatives, PSCl_2Br , PSClBr_2 , and PSBr_3 , which can only be separated by careful fractionation under low pressure.

Thiophosphoryl bromodichloride, PSCl_2Br , boils at about 80° under a pressure of 6 mm.; sp. gr. = 2.12 at 0° . When strongly cooled, it forms a white solid, which melts at -30° . It decomposes slowly in presence of water, more rapidly in contact with solutions of alkalis. Fuming nitric acid oxidises it violently, but the acid of 36° acts more slowly, and completely oxidises the sulphur and phosphorus. When heated at 100° , it decomposes into the thiophosphoryl trichloride and the chlorodibromide, the latter, in its turn, decomposing and yielding, amongst other products, thiophosphoryl tribromide.

Thiophosphoryl chlorodibromide, PSClBr_2 , boils at about 95° under a pressure of 60 mm., and has properties very similar to those of the preceding compound. When solidified it melts at -6° ; sp. gr. = 2.48 at 0° . C. H. B.

Isolation of Lithium and of Beryllium. By WILHELM BORCHERS (*Chem. Centr.*, 1895, ii, 13—14; from *Zeits. Elektrotechn. u. Elektrochemie*, 1895, 39—40).—In the treatment of minerals containing lithium, the solution of the chlorides of the alkalis and alkaline earths is made slightly alkaline and evaporated in an iron vessel, then fused with ammonium chloride to render it neutral, and electrolysed with a current of 1,000 ampères per square metre of cathode surface and 5 volts. The upper rim of the iron crucible is kept cool by the circulation of cold water, and a thin crust of solid material is formed on the surface, which prevents the metallic lithium from coming into contact with the atmosphere. The metallic globules are placed

in a paraffin bath at 130—200°, when the pure metal rises to the surface.

Beryllium chloride solutions are evaporated down with an alkali chloride and ammonium chloride, and then electrolysed in the same manner as magnesium chloride. Calcium and magnesium chlorides must not be present. The temperature must also be kept as low as possible, as otherwise the beryllium forms an alloy with the iron of the crucible.

J. J. S.

Electrolytic Silver Peroxide. By OTTOKAR SULC (*Zeits. anorg. Chem.*, 1896, **12**, 89—97).—The author has investigated the black deposit consisting for the most part of silver peroxide, which is formed during the electrolysis of silver nitrate between platinum electrodes. A platinum dish is employed as the cathode, whilst the anode consists of a piece of platinum foil cut in the form of a comb, and then rolled up. A 15 per cent. silver nitrate solution is employed, and a current of 0·06 ampère, the density at the cathode being 0·0033 ampère per centimetre. The electrolysis is allowed to continue for 3—4 hours; the silver solution, which has become contaminated with about 4 per cent. of free nitric acid, is then removed, and the electrolysis again continued. The crystalline deposit on the anode is brushed off with a glass rod and washed with water until the wash-water gives no opalescence with hydrochloric acid. The product, on analysis, gave numbers agreeing with the formula $\text{Ag}_7\text{NO}_{11}$. It forms beautiful, black octahedra, having a metallic lustre and a sp. gr. = 5·65. It is fairly stable in dry air at the ordinary temperature, and loses its lustre only after remaining some months. When quickly heated, it decomposes into a voluminous, dark brown powder, with evolution of oxygen, and this decomposition takes place with the crystalline compound at 155°, with the powdered compound at 162°. At an incipient red heat, a further decomposition takes place, red fumes are evolved, and metallic silver is formed. It is only slightly decomposed by water at ordinary temperatures, and after some time silver nitrate goes into solution; when boiled for $1\frac{1}{2}$ days with water, the silver is deposited in the form of a mirror. When boiled with alcohol, aldehyde is formed and a mirror deposited, and if a small quantity of ammonia is added, a very beautiful mirror is obtained. It is completely decomposed by oxalic acid, with evolution of carbonic anhydride, and by ammonia, with evolution of nitrogen. It dissolves in nitric acid with a dark brown coloration, and in sulphuric acid with a dirty green coloration; both solutions go colourless on heating, diluting, and on remaining. The oxygen evolved during the first decomposition which takes place, on heating, is 7·69 per cent. The percentage of nitrogen (1·40 per cent.) corresponds with a percentage of silver, as AgNO_3 , of 12·61, and this agrees with the analysis of the residue obtained by decomposing the product with hot water. Whence the author deduces the formula $3\text{Ag}_2\text{O}, \text{AgNO}_3$.

E. C. R.

Experiments with Silver Sulphide. By THEODOR GROSS (*Chem. Centr.*, 1895, ii, 353—354; from *Elektro-chem. Zeits.*, 1895,

80—81).—Silver sulphide, when brought into contact with a platinum cathode in dilute sulphuric acid, is converted into a grey mass, the gas evolved from the cathode yields, with silver nitrate solution, a greyish-black precipitate consisting of glistening plates. A similar precipitate is obtained by treating silver nitrate with electrolysed sulphuric acid. Both precipitates differ from silver sulphide, Ag_2S , in properties. The author has treated the precipitate with nitric acid, and then fused it with potash, when decomposition ensues, but its constitution has not been determined.

Silver sulphide, mixed with 3—4 times the amount of silver nitrate, then with nitric acid (sp. gr. 1.4), and evaporated to dryness and ignited, also yields a grey mass, which the author has treated with nitric acid and other reagents with no definite results (compare this vol., ii, 472). J. J. S.

Crystals produced in the Dephosphorisation of Iron. By ADOLPHE CARNOT (*Ann. des Mines*, 1895, [9], 8, 300—310; compare Abstr., 1884, 157, 520).—In the basic slags produced in the Thomas-Gilchrist process the following kinds of crystals have been found: (1) brown rectangular (orthorhombic) tablets with the composition $\text{P}_2\text{O}_5, 4\text{CaO}$; (2) brown and black hexagonal needles of much the same composition, but with 3—4 per cent. of silica; (3) brilliant, blue, orthorhombic crystals with the formula $\text{P}_2\text{O}_5, \text{SiO}_2, 5\text{CaO}$ or $\text{P}_2\text{O}_5, 3\text{CaO} + \text{SiO}_2, 2\text{CaO}$. Hilgenstock has supposed these to be trimorphous, but the differences in composition, especially as regards silica, are against this view. A new analysis has been made of the first kind of crystals, which were obtained from the basic slags of Kladno, Bohemia.

P_2O_5 .	SiO_2 .	CaO .	MgO .	FeO .	Al_2O_3 .	Total.
37.67	0.74	59.54	trace	1.44	0.37	99.76

This analysis is compared with that of similar crystals from Middlesbrough examined by Stead and Ridsdale (*Trans.*, 1887, 601). L. J. S.

Reduction in Neutral Solutions. By CARL KIPPENBERGER (*Chem. Zeit.*, 1895, 19, 1269—1270).—The author has studied the action of pure metals on carbonic anhydride solution in the absence of acids, and also on metallic carbonates, his results confirm those already published by Lieben (*Abstr.*, 1895, ii, 348). Powdered magnesium has the power of decomposing a solution of magnesium sulphate, a quantity of magnesium hydroxide corresponding with the amount of magnesium originally in solution as sulphate, is precipitated, and the metallic magnesium which was added dissolves with evolution of hydrogen. Metallic lead has a very similar action on a solution of lead nitrate. In the case of those metals whose oxides are readily reduced, no free hydrogen escapes, it being used up in the nascent states in the reduction of the metallic oxide; in other cases it is used up in the reduction of the acid radicle. For example, when metallic magnesium decomposes a solution of lead nitrate, a

small quantity of hydrogen is evolved, but the greater part is used up in the reduction of the lead hydroxide and of the nitric acid.

When a metal is added to a solution of an acid salt, the excess of acid is first decomposed, and then the acid formed by the ionisation of the normal salt. A good example of this is the decomposition of a bicarbonate solution by means of aluminium. The author states that the chemically active carbonic acid has the formula H_2CO_3 (compare Lieben, *loc. cit.*); under certain conditions small quantities of formaldehyde and formic acid can be obtained in the reduction of carbonic acid.

Magnesium, aluminium, and zinc readily reduce solutions of nitates and chlorates. In a dilute solution of a nitrate, the first reduction product is a nitrite, then hydroxylamine, and finally ammonia; these primary reduction products can, however, interact with one another to yield secondary reduction products, such as nitrous oxide, nitric oxide, nitrogen, water, &c. A chlorate is first reduced to a chlorite, but this is immediately decomposed into chloride and chlorate; this chlorate is again reduced in a similar manner, so that the final product consists almost entirely of chloride.

J. J. S.

Lead Sulphiodide. By VICTOR LENHER (*J. Amer. Chem. Soc.*, 1895, **17**, 511—513).—When hydrogen sulphide is added to a solution of $\text{PbI}_2 \cdot 2\text{KI}$, or of $\text{PbI}_2 \cdot 4\text{KI}$, in potassium iodide, a brick-red coloured precipitate is obtained; on addition of more hydrogen sulphide, the precipitate changes through dark red to brown, and finally to the black sulphide. The red precipitate was obtained pure on the addition of a saturated hydrogen sulphide solution to a strong solution of lead iodide in a saturated solution of potassium iodide. The precipitate was filtered, washed with a saturated solution of potassium iodide, then thoroughly with cold water, afterwards with absolute alcohol, with carbon bisulphide to remove any sulphur, and again with alcohol, and finally dried by drawing air over it. The substance has a great tendency to decompose into lead sulphide and lead iodide, and it is advisable to prepare only small quantities at a time. The composition is represented by the formula $\text{PbS} \cdot 4\text{PbI}_2$.

It is readily decomposed by heat, acids, alkalis, and even by long exposure to light.

J. J. S.

Enamel. By OSKAR EMMERLING (*Ber.*, 1896, **29**, 1549).—Most of the enamels used for coating iron contain silica, boric acid, alumina, and alkalis, and, if white in colour, stannic oxide. A sample of French manufacture has been found to have the percentage composition:— SiO_2 , 36.69; PbO , 52.51; K_2O , 6.33; Na_2O , 0.60; As_2O_5 , 3.74; CoO , traces; the white appearance being obtained by means of lead arsenate instead of stannic oxide. Such an enamel is readily attacked, even by dilute acids, and is obviously not to be recommended for culinary utensils.

C. F. B.

Reduction of Copper Sulphide. By DELIA STICKNEY (*Amer. Chem. J.*, 1896, **18**, 502—504).—Copper sulphide is nearly completely reduced to copper when heated in contact with the flame of a Bunsen burner.

A. G. B.

Action of Nascent Iodine on Mercuric Chloride. By M. C. SCHUYTEN (*Chem. Zeit.*, 1895, **19**, 1683).—In order to study the action of nascent iodine on mercuric chloride, the author has treated the chloride with an ethereal solution of iodoform. The two were used in molecular proportion, and were left in contact for several days in loosely stoppered bottles. Brilliant, red, octahedral crystals of mercuric iodide were obtained in almost theoretical quantity. The yield is much smaller when the iodine is not in the nascent state.

J. J. S.

Barium Tetrachromite. By E. DUFAU (*Compt. rend.*, 1896, **122**, 1125—1127).—Equal weights of chromic oxide and barium oxide are intimately mixed and heated in a crucible brasqued with barium oxide in the electric furnace in an arc from a current of 50 volts and 300 ampères for 10 minutes. The fused product, after cooling, is repeatedly treated with hydrochloric acid, and the residue is a mixture of green lamellæ of chromic oxide, and small, brilliant, black crystals of *barium tetrachromite*, $\text{BaO}_4\text{Cr}_2\text{O}_3$, which can be separated by levigation. The crystals of the tetrachromite seem to belong to the hexagonal system, and are slightly harder than quartz; sp. gr. = 5.4 at 15°.

The tetrachromite is very stable, and is slowly attacked by chlorine or bromine at a bright red heat, with formation of a barium salt and chromic oxide; iodine seems to have no action under these conditions. Water vapour at a bright red heat, and sulphur at the softening point of glass, are without action, and the tetrachromite is also not attacked by hydrofluoric, hydrochloric, nitric, and sulphuric acids. It is, however, slowly decomposed by dry hydrogen fluoride or hydrogen chloride at a red heat.

The tetrachromite is readily converted into chromate, the change taking place with incandescence in oxygen below a red heat, and also, though slowly, in air. Fused oxidising agents and alkali hydroxides and carbonates produce a similar result.

C. H. B.

Behaviour of Aluminium with Ammonium Compounds. Method of producing Chemical Change on the surface of Commercial Aluminium. By CHRISTIAN GÖTTIG (*Ber.*, 1896, **29**, 1671—1673).—Aluminium dissolves with comparative readiness in ammonia, provided the solution is sufficiently dilute, the evolution of hydrogen being readily perceptible in solutions containing only 0.025 per cent. of ammonia; the ammonium aluminate which is first formed is unstable and readily decomposes into aluminium hydroxide and ammonia. The addition of ammonium salts, or of a little acid, facilitates the solution of the metal, but in this case there is little or no evolution of hydrogen, and the surface of the metal is lighter than when ammonia alone is employed. The other constituents of commercial aluminium are not acted on by ammonia, and consequently the surface of any aluminium object, treated as above, is less readily affected by chemical or mechanical agents than the original metal.

J. B. T.

Chromium Salts. By WILLIS R. WHITNEY (*Zeit. physikal. Chem.*, 1896, **20**, 40—67).—The cause of the colour change in solutions of chromium sulphate was investigated, (1) by the alteration of conductivity on the addition of sodium or barium hydroxide, (2) by the action of the salt in effecting hydrolysis of methylic acetate. The first series of experiments indicate that one-sixth of the sulphate in the green solution is present as free sulphuric acid, and one-third as SO_4 ions, a result agreeing with Recoura's conclusion that the salt $[\text{Cr}_2\text{O}(\text{SO}_4)_4]\text{SO}_4$ is formed during the colour change. The catalytic experiments show that the green solution possesses a hydrolysing power equal to that of a mixture of one-sixth the equivalent of free acid with the corresponding amounts of the violet salt. The electrical conductivity of chromo-mono-sulphuric, -disulphuric, and -trisulphuric acids were determined, and in each case found to be equal to the conductivity of a solution of equal sulphuric acid concentration. The effects of dilute green solutions of the chloride, nitrate, sulphate, and acetate on the rate of sugar inversion were also measured in order to determine the quantity of hydrolytically dissociated acid, but owing to the unknown effect of the other ions present, accurate results were impossible. The colloidal chromo-sulphuric acid of Recoura was investigated, and as the conductivity of solutions of the composition $\text{Cr}_2(\text{SO}_4)_3 \cdot x\text{H}_2\text{SO}_4$ were always equal to those of $(x-1)\text{H}_2\text{SO}_4$ the colloidal compound is $\text{Cr}_2\text{H}_2(\text{SO}_4)_4$. The constitution of these salts, according to the theory of Werner (*Abstr.*, 1893, ii, 379) is considered, and the author points out that five out of the seven salts indicated by the theory, are known. (*See Abstr.*, 1894, ii, 382; 1893, ii, 528.)

L. M. J.

Uranium. By HENRI MOISSAN (*Compt. rend.*, 1896, **122**, 1088—1093).—The author has prepared metallic uranium (1) by the action of sodium on the double sodium uranium chloride, $\text{UCl}_4 \cdot 2\text{NaCl}$, in an iron tube, (2) by the electrolysis of the fused double chloride with carbon or iron electrodes, and a current of 8 to 10 volts and 50 amperes. The double chloride is obtained by the action of uranium chloride vapour on sodium chloride at a dull red heat, the uranium chloride being formed in the same tube by the action of chlorine on uranium carbide. Unlike the simple chloride, it is not very hygroscopic, and is practically non-volatile when fused.

The metal is, however, best obtained by mixing 500 parts of the oxide U_3O_8 with 40 parts of sugar carbon, and heating the mixture in a carbon tube, closed at one end, in an electric furnace, with a current of 800 amperes and 45 volts. The product contains a small quantity of carbon, which can be partially removed by heating it in a crucible brasqued with uranium oxide, and enclosed in a larger crucible brasqued with titanium to protect the uranium from the action of nitrogen.

When pure, uranium is white, takes a high polish, and can be worked with a file. It is not magnetic, and is much more volatile than iron. When finely divided, it decomposes water slowly at the ordinary temperature, and more rapidly at 100° . It burns in fluorine at the ordinary temperature, in chlorine at 180° , in bromine at 210° , and in iodine vapour at about 260° . It is also attacked by

hydrogen chloride and hydrogen iodide at a red heat. When finely divided, it burns in oxygen at 170° , in sulphur vapour at about 500° , and also in selenium vapour.

One of the most remarkable properties of the metal is its great tendency to combine with nitrogen. When heated in this gas at 1000° , it becomes covered with a yellow nitride, and the powdered metal decomposes ammonia above a dull red heat, with liberation of hydrogen and formation of a black, crystalline powder. C. H. B.

Tungstates and Molybdates of the Rare Earths. By FANNY R. M. HITCHCOCK (*J. Amer. Chem. Soc.*, 1895, **17**, 483—494 and 520—534).—The author has continued the investigations of Smith and Bradbury (*Abstr.*, 1892, 241), in the hopes of finding a good method for the separation of molybdic and tungstic acids. Pure sodium molybdate, $\text{Na}_2\text{MoO}_4 + 2\text{H}_2\text{O}$, was used in the experiments, and the corresponding tungstate; the latter, however, was not pure, but contained silica, ferric iron, and molybdates. It was found best not to prepare more than 250 c.c. of the tungstate solution, as it gradually attacks glass, and a sediment resembling silica is deposited. Experiments made with sodium tungstate and manganese sulphate showed that tungstic acid cannot be quantitatively precipitated from its salts by means of manganese salts.

Uranium acetate does not precipitate tungstic acid from its salts, but both uranyl nitrate and chloride precipitate the acid completely in the form of uranium tungstate, the precipitation also takes place in the presence of ammonium salts and alcohol. With a little care tungstic acid may be estimated volumetrically by means of uranyl nitrate solution, if potassium ferrocyanide is used as an indicator.

Sodium molybdate gives no precipitate with uranium acetate; with the nitrate, it yields a precipitate which almost completely dissolves on stirring. Uranyl chloride also gives a precipitate which redissolves on stirring; on standing, however, a pale lemon-yellow precipitate is formed, which goes into solution on boiling. On the addition of an excess of uranyl chloride to the cold molybdate solution, a similar yellow precipitate is obtained; it does not redissolve, but, when heated for an hour, grows denser, and gradually becomes crystalline. The crystals are insoluble in water, and after drying at 128° have the composition $\text{UO}_2 \cdot \text{MoO}_4$. The author has found it impossible to effect a complete separation between tungstic and molybdic acid by means of uranium salts.

Sodium molybdate solution gives a precipitate with cerium salts, but the amount of *cerium molybdate* thus obtained is not theoretical, as part remains in solution, the addition of alcohol completes the precipitation, but is also liable to throw down other cerium salts which may be in solution. Sodium tungstate behaves in a very similar manner with cerium salts.

Tungstates of neodymium and of *praseodymium* were obtained by treating the sodium salts with neodymium and praseodymium chloride respectively. They form gelatinous precipitates, which are very difficult to filter and wash, as they show a strong tendency to pass through the pores of the filter paper. The *molybdates* when heated gradually

become granular, and are then more easily filtered. Neodymium tungstate has a very pale rose tint before ignition, which changes to lavender colour after ignition. Praseodymium tungstate has a decided greenish-yellow tint both before and after ignition. The colours of the molybdates are similar to those of the tungstates, but deeper in tint. With the praseodymium salts, the solubility increases with a rise in temperature, but with neodymium tungstate, the solubility decreases as the temperature rises. Details as to analyses are given.

The precipitation of both molybdic and tungstic acids by neodymium chloride is practically quantitative, whereas that of molybdic acid with praseodymium chloride is not.

Sodium tungstate solution yields with lanthanum chloride, in the presence of alcohol, a precipitate, which, on drying, has a delicate blue colour.

J. J. S.

Zirconium Sulphite. By FRANK P. VENABLE and CHARLES BASKERVILLE (*J. Amer. Chem. Soc.*, 1895, **17**, 448—453).—The authors have not succeeded—except in one case—in obtaining any zirconium sulphite corresponding with the acid, or normal, salts, only indefinite compounds or mixtures of the sulphite with the hydroxide have been prepared. A $2\frac{1}{2}$ per cent. solution of the pure chloride, neutralised with ammonia and then saturated with sulphurous anhydride, yields a white precipitate, which, after a time, redissolves; if the clear solution thus obtained be diluted with several times its volume of water and then boiled, a heavy, white precipitate is produced. When dried and powdered, it resembles finely divided silica; the ratio of zirconium to sulphurous anhydride was 2 : 1.

Freshly prepared zirconium hydroxide was also treated with a concentrated solution of sulphurous anhydride and kept for three months, with occasional shaking, a layer of gelatinous hydroxide was deposited on the bottom of the vessel, and upon this a white, finely divided substance formed.

The white layer was analysed, and the ratio of zirconium to sulphurous anhydride was found to be 2·2 : 1.

The supernatant liquor was found to contain zirconium, and when evaporated over sulphuric acid, gave a small quantity of hard, white nodular crystals, in appearance resembling zirconium sulphate. The results of analysis proved them to be a hydrated sulphite, $\text{Zr}(\text{SO}_3)_2 + 7\text{H}_2\text{O}$.

The precipitate obtained by boiling a solution of the chloride with a solution of sodium sulphite was also analysed. The ratio of zirconium to sulphurous anhydride was found to be 4 : 1. No definite thiosulphate could be obtained by treating the chloride with sodium thiosulphate under varying conditions.

J. J. S.

Action of Air and Nitric Peroxide on some Halogen Bismuth Compounds. By V. THOMAS (*Compt. rend.*, 1896, **122**, 1060—1062).—When heated gently in nitric peroxide, bismuth tribromide is converted into small, very brilliant, white lamellæ of the oxybromide BiOBr . No further loss of bromine takes place, even at a high temperature. If heated strongly in air, however, it loses bromine, and is only very imperfectly converted into the oxide

When the tribromide is heated with free exposure to air, the greater part volatilises, and the residue consists of the oxybromide. The triiodide, when heated in nitric peroxide, is first converted into the oxyiodide, and subsequently into the oxide, and the same products are formed.

Bismuth dichloride, obtained by the action of chlorine on the metal, is a black, crystalline mass, which is converted into the oxychloride by nitric peroxide in the cold, although a gentle heat accelerates the reaction. When heated in presence of air, a large part of the dichloride volatilises, but the residue has the composition and properties of the oxychloride, BiOCl . (Compare Abstr., 1895, ii, 495.)

C. H. B.

Precipitation of the Sulphides of Platinum : Colloidal Platinic Sulphide. By UBALDO ANTONY and ADOLFO LUCCHESI (*Gazzetta*, 1896, 26, i, 211—218).—The whole of the metal is precipitated from a 3 per cent. aqueous solution of hydrogen platinochloride by hydrogen sulphide at 90° as pure platinic sulphide, PtS_2 ; for analytical purposes, the precipitate should be collected and washed in an atmosphere of hydrogen sulphide, and dried in nitrogen at 70 — 80° . The sulphur cannot be estimated by the authors' modification of Carius's method (Abstr., 1890, 1216), owing to the formation of barium platinochloride, which is not easily separated from the barium sulphate, nor by treatment with chlorine and bromine, for then halogen compounds of platinum volatilise, as in the case of iridium (Abstr., 1893, ii, 379).

At ordinary temperatures (15 — 18°) a mixed yellow and brown precipitate is slowly thrown down by hydrogen sulphide from the hydrogen platinochloride solution, and the supernatant liquid remains red; the mixed precipitate continually loses hydrogen sulphide on heating, and ultimately yields platinic sulphide at 200° . The brown and yellow precipitates are possibly platinic hydrosulphides.

The reddish mother liquor contains colloidal platinic sulphide, which is slowly deposited even at 0° . A 0.5 per cent. aqueous solution of hydrogen platinochloride gives no precipitate at 15 — 18° with hydrogen sulphide, but only a red-brown coloration; no precipitate is obtained on boiling, but on adding hydrochloric acid, the solution deposits platinic sulphide, and becomes decolorised. The precipitation of platinic sulphide from the more concentrated solution at 15 — 18° thus seems due to the action of the liberated hydrochloric acid.

W. J. P.

Mineralogical Chemistry.

Hyacinth (Quartz) in Gypsum, near Jena. By E. ZSCHIMMER (*Tsch. Min. Mitth.*, 1896, **15**, 457—465).—Small, red, doubly-terminated crystals of quartz occur with small crystals of dolomite in gypsum bands in the Trias beds near Jena; they enclose gypsum, and probably also anhydrite. Experiments show that silica is fairly

soluble in a solution of magnesium hydrogen carbonate (10 litres containing 1·3342 gram SiO_2 , and 15·191 grams MgCO_3), and that, when calcium sulphate is added to this solution, about 35 per cent. of the silica is deposited. The origin of the quartz crystals in the gypsum is therefore attributed to the action of such a solution on beds of anhydrite.

L. J. S.

A new Cobalt Mineral. By PABLO MARTENS (*Actes Soc. Sci., Chili*, 1895, 5, 87—88).—The mineral is black and amorphous; streak, black; fracture, conchoidal; sp. gr., 3·39; $H = 3\cdot5$. With hydrochloric acid it gives off chlorine; over sulphuric acid some water is lost. Analysis gave

Co.	Cu.	SiO_2 .	Fe_2O_3 .	H_2O (hygroscopic).	H_2O (combined).	O [diff.].
46·76	12·65	1·76	0·29	4·92	14·08	[19·54]

This agrees with $\text{CuO}\cdot2\text{CoO}\cdot\text{Co}_2\text{O}_3 + 4\text{H}_2\text{O}$. The exact locality is not known, but is probably in the north of Chili. The mineral is named *Schulzenite*, after J. Schulze, in whose collection it was found.

L. J. S.

Formation of Tin Veins. By FERDINAND GAUTIER (*Actes Soc. Sci., Chili*, 1895, 5, 82—84).—From the non-occurrence of minerals containing fluorine in the cassiterite veins of some districts of Bolivia, the author supposes the tin dioxide to have been formed by the interaction of water vapour and tin chloride. The cassiterite of another Bolivian locality shows impressions of quartz crystals; this seems to imply that there has been interaction between water vapour and tin fluoride, the quartz being acted on by the hydrogen fluoride formed, and removed as silicon fluoride; minerals containing fluorine are, however, in this case also absent.

L. J. S.

Origin of Nitrates in Griqualand West. By R. MARLOTH (*Trans. S. African Phil. Soc.*, 1896, 8, 113—118).—Under cliffs and in caves in the Asbestos Mountains and the Doornbergen of S. Africa, there are deposits of nitrates, which have their origin in the nitrification (by microbes) of animal refuse, principally the fæces of rock rabbits; the potassium has partly been supplied by the animal matter, and partly derived from the associated rocks. The deposits contain calcium sulphate, indicating that the potassium nitrate has been formed by the interaction of calcium nitrate and potassium sulphate.

L. J. S.

Aluminium and Potassium Phosphates. By ADOLPHE CARNOT (*Ann. des Mines*, 1895, [9], 8, 311—320).—An analysis of a specimen of "minervite," from Dept. Hérault, very similar in appearance to the aluminium and potassium phosphate from the cavern of Tour-Combes, Oran (this vol., ii, 34), gave the following results, which are almost the same as those obtained for the mineral from the latter locality, but which differ, especially in the presence of potassium, from those shown in Gautier's analysis of the minervite of Hérault (*Abstr.*, 1893, ii, 419, 577). The author, therefore, considers minervite, not as a hydrated phosphate of aluminium alone, but of aluminium

and potassium, in which part of the aluminium is replaced by iron, and part of the potassium by ammonium, calcium, and magnesium.

P_2O_5 .	Al_2O_3 .	Fe_2O_3 .	K_2O .	CaO .	MgO .	NH_4 .	H_2O (at 180°).
37.28	18.59	0.83	8.28	1.40	0.33	0.52	23.70

Loss from
 180° to redness.
4.50

Sand, &c.
4.35

F, Cl, SO_3 .
traces

Total.
99.78

Formula, $P_2O_5 + 0.70(Al, Fe)_2O_3 + 0.25(K, Am, Ca, Mg)_2O_2 + 5.40H_2O$. This is nearly the composition of a mixture of Al_2O_3, P_2O_5 , with mono- and di-basic phosphates of the other bases.

L. J. S.

Thaumasite. By FÉLIX PISANI (*Bull. Soc. fran. Min.*, 1896, 19, 85—87).—The thaumasite from Paterson, New Jersey, recently described by Penfield and Pratt (this vol., ii, 367), has been analysed, the more crystalline portion being used.

SiO_2 .	CO_2 .	SO_3 .	CaO .	H_2O .	Al_2O_3, Fe_2O_3 .	Total.
8.95	8.25	12.60	27.30	43.70	0.30	101.10

This gives the formula $2CaO, 2(SiO_2, CO_2) + CaO, SO_3 + 16H_2O$, there being here slightly less silica, and slightly more carbonic anhydride and water than in the Swedish mineral. Dilute hydrochloric acid easily decomposes it, and water dissolves out traces of calcium sulphate. There is practically no loss at 100° . Under the microscope, the mineral appears homogeneous, and to be monosymmetric; it is to be considered as a definite species.

L. J. S.

Pickeringite from New South Wales. By GEORGE W. CARD (*Records Geol. Survey, N.S.W.*, 1896, 5, 6—14).—Pickeringite, as aggregates of delicate silky fibres, gave analysis I (by J. C. H. Mingaye) for material from Capertee, and II (by White) for material from the Shoalhaven district.

Al_2O_3 .	MgO .	K_2O .	Na_2O .	SO_3 .	Insol.	Water [diff.].
I. 7.14	9.03	0.32	0.53	35.68	1.51	[45.79]
II. 10.91	4.68	1.06	trace	38.14	1.74	[42.37]

In II, the percentage of magnesia is normal, but in I it is unusually high (compare this vol., ii, 251). It seems likely that many of the magnesium alums, which have been described under various names, are not homogeneous.

Various minerals and rocks from New South Wales are shortly described in the paper.

L. J. S.

A Blue Mineral, supposed to be Ultramarine, from New Mexico. By R. L. PACKARD (*Proc. U.S. National Museum*, 1895, 17, 19—20).—A blue, earthy mineral, which, when first found, was supposed to be ultramarine, occurs as irregular veins in the limestone carrying the silver ore at Chloride Flat, near Silver City, New Mexico. The material, after being purified as far as possible by

hydrochloric acid and sodium carbonate solution, gave the following results on analysis.

Ignition.	SiO ₂ .	MgO.	FeO.	Al ₂ O ₃ .	K ₂ O.	Na ₂ O.	Total.
6.47	62.43	28.53	0.99	0.25	0.14	0.16	98.97

Chemically it is, therefore, like talc, but it differs from the latter in physical properties. L. J. S.

Synthesis of Topaz. By ALFRED REICH (*Monatsh.*, 1896, 17, 149—171).—The contradictory results obtained by Daubrée and St. Claire Deville have led the author to again attempt the preparation of fluorine compounds by the action of silicon fluoride on aluminium silicate.

Amorphous aluminium silicate, having approximately the composition Al_2SiO_5 , was obtained by adding aluminium sulphate solution to a solution of sodium silicate and caustic soda, the precipitate being subsequently washed by decantation and dialysis; this, after calcination, was heated to bright redness in a current of carefully dried silicon fluoride. The silicate increased in weight by 42.4—43.1 per cent., and the product consisted of indefinite, doubly refracting, seemingly rhombic crystals, which gave on analysis, in parts per cent., SiO_2 , 42.24—42.46; Al_2O_3 , 44.54—45.17, and F_2 , 22.06.

A crystalline aluminium silicate, made by a modification of Frémy and Feil's process (*Abstr.*, 1878, 203), consisted of a mixture of corundum with andalusite or sillimanite; the various preparations made contained in parts per cent., SiO_2 , 5—24; and Al_2O_3 , 75—95, but all, when heated in silicon fluoride, increased by 33—38 per cent. in weight, yielding products, which gave on analysis, SiO_2 , 31.70—33.04; Al_2O_3 , 55.01—57.03; and F_2 , 18.17—20.09, or, approximately, $\text{Al}_2\text{SiF}_2\text{O}_4$. The numbers are so nearly identical with those given by topaz that the substance must be considered as artificial topaz. The few crystallographic measurements possible with the artificial crystals also agree very closely with those of the mineral. On strongly heating the artificial crystals, a product of the percentage composition SiO_2 , 29.56, and Al_2O_3 , 67.95, results; these numbers are practically identical with those given by the product of heating natural topaz. Silicon fluoride cannot be the only substance driven off by heat, aluminium fluoride or fluorine must also be volatilised.

The author has not succeeded in obtaining concordant results with Jannasch's method (*Abstr.*, 1895, ii, 460) of analysing silicates containing fluorine, and recommends the following process. A mixture of 4—6 parts of sodium hydroxide with one of the silicate is fused in a silver crucible for 10—15 minutes; the product is then dissolved in water and precipitated by carbonic anhydride. The liquid is evaporated to a small bulk with ammonium carbonate, and three or four successive quantities of ammonium carbonate added and evaporated off. Warm water is then added, and the precipitate filtered on a platinum funnel and washed with ammonium carbonate solution; the precipitate contains all the alumina and silica, and a little silver, which are separated, and the former two constituents estimated in

the usual way. The filtrate is evaporated to drive off ammonium carbonate, acidified with acetic acid, rendered alkaline with lime water, evaporated to dryness, the residue taken up with water, and the solution filtered. The precipitate is lightly calcined and treated with dilute acetic acid; the calcium fluoride is weighed as such, then treated with sulphuric acid, and weighed as calcium sulphate as a control.

W. J. P.

[**Phillipsite from Wingendorf, Prussian Silesia.**] By P. KRUSCH (*Jahrb. k. Preuss. Geol. Landesanst. und Bergakad.*, 1895, **15**, (1894), 312—314).—In a description (p. 279—324) of the basalts occurring between Neisse and the River Queiss, Prussian Silesia, an analysis (by Klüss) is given of phillipsite from the basalt of Wingendorf, near Lauban. The rock here is especially rich in zeolites; phillipsite occurs as water-clear, twinned crystals.

Al ₂ O ₃ .	CaO.	K ₂ O.	Na ₂ O.	H ₂ O (at 100°).	H ₂ O (at 200°).	H ₂ O (on ignition).	SiO ₂ [diff.].
19·92	4·74	6·34	1·72	3·86	6·44	6·37	50·61

L. J. S.

Felspars of Igneous Rocks. By FERDINAND FOUQUÉ (*Zeits. Kryst. Min.*, 1896, **26**, 300—316; from *Bull. Soc. fran. Min.*, 1894, **17**, 283—611).—Optical and chemical determinations, both made on the same material, are given of numerous felspars from various rocks; the former include the extinctions in sections perpendicular to *a* and *c*, and on *c*(001) and *b*(010), the optic axial angle, the indices of refraction, &c. The following analyses of homogeneous material, separated by means of methylenic iodide, are given: I, anorthite from Etna; II—IV, labradorite-bytownite from the Azores; V, do. from Besseyre, Haute-Loire; VI—VIII, labradorite from the Azores; IX, andesine from Chenavary, Ardèche; X—XI, do. from Arcuentu, Sardinia; XII, oligoclase-andesine from Alagnon, Haute-Loire;

	SiO ₂ .	Al ₂ O ₃ .	CaO.	Na ₂ O.	K ₂ O.	MgO.	Fe ₂ O ₃ .	Total.	Sp. gr.
I ...	44·1	37·8	18·6	0·9	—	—	trace	100·4	2·748
II ...	53·4	29·4	12·5	4·8	0·2	—	—	100·3	2·710
III ...	54·2	30·3	11·8	3·9	0·2	—	—	100·4	2·705
IV ...	53·3	30·1	11·4	5·1	0·1	0·1	trace	100·1	2·705
V ...	54·5	29·8	11·4	4·5	0·3	—	—	100·5	2·698
VI ...	55·4	29·4	9·7	5·7	—	0·2	0·5	100·9	2·695
VII ...	55·9	29·3	9·7	5·0	0·3	—	—	100·2	2·698
VIII ...	54·9	29·3	10·25	5·35	0·07	0·06	0·6	100·53	2·696
IX ...	58·65	26·50	8·41	6·09	0·37	—	—	100·02	{ 2·662- 2·685
X ...	62·65	24·19	6·28	6·48	1·24	—	—	100·74	—
XI ...	63·80	23·43	6·26	5·58	1·44	—	—	100·51	—
XII ...	62·4	22·8	7·00	8·4	0·5	—	—	101·1	2·612
XIII ...	64·32	23·05	3·90	8·50	0·54	—	—	100·31	2·642
XIV ...	68·2	19·0	—	13·5	—	—	—	100·7	2·624
XV ...	67·9	19·4	2·4	10·9	0·3	—	—	100·9	2·592
XVI ...	67·7	19·7	0·7	11·1	1·7	—	—	100·9	2·597
XVII ...	67·8	20·0	0·6	10·5	1·3	—	—	100·2	2·608
XVIII ...	67·67	19·45	0·47	9·21	3·95	—	—	100·75	2·572
XIX ...	68·3	19·5	trace	7·1	5·7	—	—	100·6	2·585
XX ...	66·9	19·8	1·3	7·6	4·5	—	—	100·1	2·567
XXI ...	68·0	20·1	0·6	10·1	1·2	—	—	100·0	—

XIII, oligoclase from Mexico?; XIV, albite from Modane, Savoy; XV, albite from Albepeyre, Haute-Loire; XVI—XVIII, anorthoclase from the Azores; XIX, do. from Sardinia; XX, do. from Mont Dore; XXI, do. from Liberté, Haute-Loire.

The author is led to the conclusion that the rock-forming anorthic feldspars are represented by the following types of definite composition, between which there are no intermediate members, but which may intergrow with one another; this is opposed to Tschermak's theory of a mixed series. Several of these types usually occur together in the same rock, the later ones being the more acid.

	Sp. gr.	SiO ₂ per cent.	2V.	Optical sign.	Extinction on		β_{Na}
					c(001).	b(010).	
Anorthite.....	2·745	44	77° 30'	—	—36° 30'	—41° 30'	1·582
Bytownite.....	2·725	—	—	—	—	—	—
Labradorite-bytownite..	2·705	54	77	+	—11	—25	1·563
Labradorite.....	2·696	55	77	+	—5 30	—20	1·558
Andesine.....	2·675	58	88	+	—2 30	—10	1·553
Andesine-oligoclase....	2·654	62	86	—	—2	—4	—
Oligoclase.....	2·645	64	88	—	+ 2	+ 8	1·542
Oligoclase-albite.....	2·640	65	88 30	+	+ 2 30	+10 30	—
Albite.....	2·610	68	77	+	+ 4	+19 30	1·534
Anorthoclase.....	2·580	68	45	—	+ 2	+ 9	1·528
Microcline-anorthoclase	2·570	—	60	—	—	—	—
Microcline.....	2·560	65·5	88	—	+15 30	+ 5 30	1·526

The following analyses are also given: I, yellow-brown hornblende from biotite-hornblende-andesite from Lioran; II, biotite from biotite-obsidian from the Plomb du Cantal.

	SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	FeO.	MgO.	CaO.	Na ₂ O.	K ₂ O.	Total.
I.	41·3	15·6	11·5	3·2	13·5	13·1	1·4	0·3	99·9
II.	43·4	20·4	9·1	—	17·1	1·7	0·2	8·6	100·5

L. J. S.

Mica-syenite from Rothsönberg, Saxony. By J. M. C. HENDERSON (*Zeits. deutsch. geol. Ges.*, 1895, **47**, 534–547).—A dyke rock containing orthoclase, plagioclase, biotite, muscovite, quartz, magnetite, apatite, calcite, and pyrites from Rothsönberg, near Deutschenbora, in the Kingdom of Saxony, gave analysis I; the structure is panidiomorphic-granular, so that the rock is called a mica-syenite rather than a lamprophyre. Analysis II is of the feldspar of sp. gr. 2·62–2·63; although apparently fresh, it is kaolinised, as is seen under the microscope and by the water in the analysis.

	SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	CaO.	MgO.	K ₂ O.	Na ₂ O.	H ₂ O.	CO ₂ .	S.	Total.
I.	57·63	16·47	5·37	5·25	4·44	3·12	5·15	0·45	2·14	0·95	100·97
II.	66·67	16·81	0·97	2·06	0·54	4·82	5·89	1·80	0·25	—	99·81

L. J. S.

[Analyses of Sericite, Augite, and Waters from Bohemia.] By J. E. HIBSCH (*Tsch. Min. Mitth.*, 1895, **15**, 201—290).—In a paper explanatory of the geological map of the Bohemian Mittelgebirge are given several analyses of rocks, together with the following of minerals and waters. I is the mean of two analyses of sericite from a sericite-albite-gneiss, near Tetschen. II (by R. Pfohl) is of augite from a leucite-tephrite containing nepheline from Falkenberg; sp. gr., 3·37.

	SiO ₂ .	TiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	FeO.	CaO.	MgO.	K ₂ O.
I.	47·85	—	35·86	3·12	—	0·55	0·25	8·56
II.	45·67	0·62	9·04	7·46	2·00	21·78	12·09	0·56
			Na ₂ O.	H ₂ O.	Total.			
			I. 0·54	0·51	101·24			
			II. 1·25	0·31	100·78			

Water from a spring near Liebwert, east of Tetschen, gave III in 100,000 parts; from a spring near Gomplitz, IV; both analyses by F. Ullik.

	CaO.	MgO.	K ₂ O.	Na ₂ O.	Al ₂ O ₃ , Fe ₂ O ₃ .	Cl.	SO ₃ .
III.	5·05	1·28	0·37	2·03	0·18	0·64	0·82
IV.	14·67	2·33	0·28	0·93	0·26	0·71	0·21
			SiO ₂ .	NH ₃ .	N ₂ O ₃ .	Reduced KMnO ₄ .	CO ₂ .
III.			4·50	trace	trace	0·12	6·35
IV.			1·65	trace	trace	0·27	19·9

L. J. S.

Serpentine after Amphibolite. By JOHN B. JAQUET (*Records Geol. Survey, N.S.W.*, 1896, **5**, 18—25).—A description is given of the intrusive and metamorphic rocks of Berthong, Co. Bland, N.S.W.; the ultrabasic rocks include an amphibolite, which consists of hornblende, with a little magnetite and, rarely, chromite; this has been altered in places to serpentine, as is seen by the intimate association of the two rocks, and by the microscopical examination. The serpentine, which contains magnetite and chromite, gave analysis I, and the adjacent amphibolite, analysis II (by J. C. H. Mingaye). The alteration has been accompanied by a removal of alumina and silica.

	SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	FeO.	MnO.	Cr ₂ O ₃ .	(Co,Ni)O.	CaO.	MgO.
I.	40·80	2·54	6·20	0·48	trace	0·29	0·25	—	32·82
II.	49·30	10·42	2·20	3·83	—	trace	trace	11·82	19·36
					H ₂ O	H ₂ O			
					(at 110°).	(combined).	Total.	Sp. gr.	
I.					2·87	10·11	99·63	2·52	
II.					0·26	0·79	99·62	3·00	

L. J. S.

A Mineral Spring at Bungonia. By J. MILNE CURRAN (*Jour. and Proc. Roy. Soc., N.S.W.*, 1894, **28**, 54—59).—Analysis of the water of a spring at Bungonia, New South Wales, gave the following results in grains per gallon: SiO₂, 1·47; FeO, 0·19; CaO, 35·00;

MgO, 5.18; Na₂O, 5.53; K₂O, 4.27; Cl, 5.88; SO₃, 1.16; CO₂ (combined), 34.86; H₂O (combined), 10.75 = total solids, 104.29 (less oxygen for Cl = 103.04).

Carbonic anhydride is given off by the water with deposition of a tufa, either porous or compact and crystalline, which gave on analysis,

Insol. in HCl.		Fe ₂ O ₃ , Al ₂ O ₃ .	CaCO ₃ .	MgCO ₃ .	Na ₂ CO ₃ , K ₂ CO ₃ .
Organic matter.	SiO ₂ .				
7.9	3.6	0.9	79.4	2.3	1.0
H ₂ O (combined).		Total.		Sp. gr.	
4.9		100.0		2.58	

L. J. S.

The new hot Springs of Ædipsos and Gialtra. By ANASTASIOS K. DAMBERGIS (*Tsch. Min. Mitth.*, 1896, **15**, 385—393).—During the Locris (Greece) earthquakes of April, 1894, more than one hundred new hot springs were started at Ædipsos and Gialtra, whilst the old ones were affected as regards quantity of water and temperature, there being an increase in most cases. The new springs are of the same nature as the old ones, the temperature varying from 32° to 82°; determinations of the total solids, chlorine, and carbonic anhydride (in grams per litre) are given for several springs, the extremes of which are given below, and compared with the extremes obtained for the old springs in 1889 (*Abstr.*, 1892, i, 418) and 1894. The vapour of many of the new springs smells of hydrogen sulphide, as does that of the old springs; only in one case was there a determinable amount of hydrogen sulphide, however, namely, 21.7 c.c. in a litre of water.

	Total solids.	Chlorine.	Carbonic anhydride.
New springs of Ædipsos ...	19.188—37.327	12.699—21.300	0.601—0.698
" " Gialtra	37.505—39.149	18.083—19.380	0.656—0.692
Old springs of Ædipsos (1889)	22.958—33.355	13.119—19.230	0.561—0.673
" " " (May, 1894)	29.580—39.707	15.655—19.241	—

L. J. S.

Physiological Chemistry.

Influence of Fat and Starch on Metabolism. By A. WICKE and HUGO WEISKE (*Zeit. physiol. Chem.*, 1896, **22**, 137—152).—In this second series of experiments, the same two sheep were employed as on a previous occasion (*Abstr.*, 1895, ii, 516).

The daily diet was 800 grams of air-dried hay and 200 grams of linseed; this was continued for eight days, the urine and fæces being

examined every day. During a second period, in addition, 146.4 grams of starch, and during a third period an equivalent quantity (in heat value, 60 grams) of olive oil was given.

In both cases the amount of nitrogen excreted was lessened, but this proteid sparing action was much more marked in the starch than in the fat periods.

W. D. H.

Nutritive value of Gland-peptone. By ALEXANDER ELLINGER (*Zeit. Biol.*, 1896, **33**, 190—218).—Most previous observers have stated that various commercial preparations of "peptone" are of equal nutritive value to that of native proteid. Voit, however (*Hermann's Handbuch*, **6**, 121), did not find this to be the case in dogs with the form of peptone he used. The different kinds of so-called peptone used account in some degree for this difference in result. The present research was also carried out on dogs. The peptone chiefly investigated was gland-peptone, an antipeptone of low molecular weight, formed by the auto-digestion of the pancreas. This, in contrast to albumin and Witte's peptone (chiefly albumoses), does not maintain nitrogenous equilibrium; the animal loses weight, and gets ill. It is suggested that the intestinal epithelium is not able to reconvert such large doses of peptone of low molecular weight into albumin, but that some is absorbed as such, and produces harmful results.

W. D. H.

Absorption of Proteids in the Small Intestine. By GEORG FRIEDLÄNDER (*Zeit. Biol.*, 1896, **33**, 264—287).—Physiologists have lately arrived at the conclusion that mere physical reasons will not explain absorption in the alimentary canal; and in special connection with proteids, that their change into peptone before absorption is not absolutely necessary. Proteids, when in excess, are absorbed unchanged, and appear in the urine. They usually undergo some change, either before or during their passage through the mucous membrane, so that, even if they are not peptonised, they cannot be recognised in their original form afterwards. In the present research, known quantities of proteid in solution were injected into isolated loops of intestine a considerable distance from the pylorus, and their contents were subsequently examined, allowance being made for any proteid matter from the intestinal wall. In the following table the mean percentage of proteid absorbed is given for a number of different proteids used in the experiments.

Casein	0
Acid-myosin	0
Acid-albumin	0
Egg-albumin and serum albumin	21
Alkali-albumin	69
Albumoses	72
Peptone	91

W. D. H.

Molybdic acid as a Microscopic Reagent. By L. HEINE (*Zeit. physiol. Chem.*, 1896, **22**, 132—136).—Lilienfeld and Monti's (Abstr.,

1893, ii, 135) method for microchemically localising phosphorus is not regarded as trustworthy. The reduction, either by pyrogallol or by stannous chloride, as some recommend, occurs in structures and substances which are free from phosphorus. W. D. H.

Thymin from the Spermatozoa of the Sturgeon. By ALBRECHT C. L. M. L. KOSSEL (*Zeit. physiol. Chem.*, 1896, **22**, 188—190).—Thymin, previously prepared from the nuclei of the thymus, is also obtainable as a decomposition product of the nucleic acid of the spermatozoa of the sturgeon. W. D. H.

Hæmatoporphyrinuria. By BAREND J. STOKVIS (*J. Pathol. and Bacteriol.*, 1896, **4**, 155).—The author previously considered that the hæmatoporphyrin in normal urine and in that of patients taking sulphonal, was due to the presence of blood in the alimentary canal (*Zeit. f. Med.*, **27**, 1). Garrod and Hopkins (this vol., ii, 264) doubted this explanation, and it is now withdrawn, because the urine of rabbits contains the material when they are feeding on blood-free food, and living under conditions which exclude hæmorrhages. W. D. H.

Chemistry of Vegetable Physiology and Agriculture.

Proteïds and Carbohydrates of Green Leaves as Products of Assimilation. By W. SAPOSCHNIKOFF (*Bied. Centr.*, 1896, **25**, 106—108; from *Bot. Centr.*, 1895, **62**, 246; compare *Abstr.*, 1891, 763; *Bied. Centr.*, 1893, 70, and 1894, 775).—The results of experiments, in which cut leaves of *Vitis vinifera* and *V. labrusca* were kept in a nutritive solution and in distilled water respectively, showed that with plenty of nitrate and a moderate amount of light, there is an increased production of proteïds with lessened formation of carbohydrates, or the production of carbohydrates may be quite suppressed. Asparagine cannot serve as a source of nitrogen for producing proteïds in cut leaves.

In an atmosphere rich in carbonic anhydride, the production of carbohydrates is increased, even when light is unfavourable, but there is no increased production of proteïds.

When entire plants are kept in the dark, there is not only a migration of carbohydrates, but also, although to a less extent, of proteïds from the leaves.

The maximum accumulation of different substances in cut leaves, of which the stalks dipped in water or nutritive solutions, was as follows: Carbohydrates, in the two varieties of *Vitis* = 23—29 per cent.; sugar = 5·2 per cent.; starch = 8 per cent. of the dry matter. In leaves of *Rubus cæsius* and *fruticosus* the maximum for sugar was found to be between 6 and 7 per cent.

N. H. J. M.

The Position of Arsenic in Plant Production. By JULIUS STOKLASA (*Bied. Centr.*, 1896, **25**, 353; from *Chem. Rep.*, 1896, 16).—A number of plants, 35 days' old, were treated with nutritive solutions containing (1) 0.019 gram of arsenious acid, (2) 0.023 gram and (3) 0.23 gram of arsenic acid. In solution (2) there was no poisoning; in solution (1) the plants were killed in 46 to 90 hours; in solution (3) in 24–42 days.

Further experiments with oats showed that arsenic acid cannot take the place of phosphoric acid, but that, in absence of phosphoric acid, it will induce increased production of organic substance up to the flowering period. N. H. J. M.

The Tannin of Fungi. By OTTO NAUMANN (*Bied. Centr.*, 1896, **25**, 353; from *Bot. Centr.*, 1896, **65**, 254, and *Inaug. Diss.*, Erlangen).—Fungi cannot produce tannin, but may take it up and utilise it as food when decomposed. Certain fungi do not absorb tannin, and are injured in presence of excessive amounts. *Polyporeæ* contained 0.034 to 0.400 per cent. of tannin; *Agaricaceæ*, 0.041 to 0.060 per cent. Parasites usually contained more tannin (0.180–0.400 per cent.). The relatively small amounts of tannin in fungi as compared with various plants confirms Hartig's view, that in fungi the tannin is chemically decomposed. N. H. J. M.

Nutrition and Formation of Substance in Sugar Beet in the Second Year of Growth. By FRIEDRICH STROHMER, H. BRIEM, and A. STIFT (*Bied. Centr.*, 1896, **25**, 170–172; compare *ibid.*, 1893, **22**, 473).—The experiments now recorded were made with entire roots instead of with half roots. The mineral and organic matters of a root are not sufficient for the production of leaves and stems, &c., so that application of nutritive matter is necessary, if it is not already present in the soil in an assimilable state. In the second year of growth, the newly produced substance of the whole plant shows a gradual decrease of non-nitrogenous extract, mainly due to a gradual decrease of this substance in the dry matter of the root. The dry matter of the developing plant, however, shows a gradual increase of crude fibre, nitrogen, and ash constituents. Mineral matter is taken up by the root in the first period of growth. The object of the nitrogen-free reserve substance seems chiefly to provide for the heat necessary for growth. Nitrogen is of most importance for the production and character of seed. Proteids, as well as the nitrogen-free extract substances, seem to have the same physiological function in the life of plants as in animals. N. H. J. M.

The Nutritive Substances of Beetroot. By W. SCHNEIDEWIND and H. C. MÜLLER (*Bied. Centr.*, 1896, **25**, 315–326; from *J. Landw.*, 1896, **44**).—By cultivation and selection of beetroot for sugar, the amount of ash in the roots was often reduced to little more than half the average amounts given by Wolff, whilst the amount of ash in the leaves was not influenced. The amounts of ash and of nitrogen are in inverse proportion to the amount of sugar, the composition of the ash also being of importance. Potash manures and sodium nitrate

increase the percentage amounts of potassium and sodium respectively in roots and leaves, and also the total amounts. Kainite increases the taking up of potash but not of soda or magnesia. Manuring with lime gives rise to increased amounts of lime in the plants, but the lime is diminished by applications of potash and soda.

Manuring with kainite can increase assimilation of phosphoric acid, but without benefit as regards sugar production. A further effect of kainite is to increase assimilation of chlorine, which is mainly stored up in the leaves; this seems to be beneficial, owing to the plant acids being diminished as the chlorine increases.

Late application of nitrogen is not recommended; luxuriance of leaves should be obtained as early as possible. Sodium nitrate acts, however, more quickly than potassium nitrate (owing to its being more readily soluble and diffusible), and may be applied as an early top dressing with greater effect than before sowing.

The mutual influence of single nutritive substances has an important role in plant life, and should be investigated under different conditions of soil, &c.

N. H. J. M.

Amount of Acid in Rhubarb Stems and in Rhubarb Wine.

By R. OTTO (*Bied. Centr.*, 1896, **25**, 128—129; from *Landw. Jahrb.*, 1895, **24**, 273).—The microchemical examination of rhubarb stems showed the presence of calcium oxalate, in some varieties in large quantities. The following amounts of free oxalic acid were found in different varieties of rhubarb stems at the flowering period (17 and 18 May):—Prince of Wales, 0.1913; Queen Victoria, 0.1943; *Rheum nepalense*, 0.2153; *R. paragon*, 0.2230; and *R. nutans*, 0.3161 per cent. On the 4th June, the following percentages were found:—*R. crispum*, 0.2080; *R. leucorhizum*, 0.2220; *R. palmatum*, 0.2580; *R. nepalense*, 0.2710.

Rhubarb wine, as prepared from the stems, had the following composition (grams per 100 c.c.).

Extract.	Alcohol.	Acid.	Glycerol.	Oxalic acid.	Ash.	Sp. gr. at 15°.
2.412	3.94	0.748	0.547	0.0670	0.397	1.0005

The oxalic acid is very readily removed by adding precipitated calcium carbonate (in this case 0.72 gram per litre).

N. H. J. M.

Identification and Isolation of Acids contained in Plants.

By LÉON LINDET (*Compt. rend.*, 1896, **122**, 1135—1137).—Methylic alcohol of 95° G.L. dissolves only 0.3 per cent. of quinine hydrogen citrate and 3.3 per cent. of the normal salt, but it dissolves 8.2 per cent. of quinine hydrogen malate and 8.0 per cent. of the normal salt. It also dissolves 9.2 per cent. of quinine hydrogen oxalate, and 8.2 per cent. of the normal oxalate.

A methylic alcohol solution of cinchonine, precipitates malic acid in the same circumstances as quinine precipitates citric acid, the solubility of cinchonine hydrogen malate being only 2.5 per cent. All the other salts of cinchonine with vegetable acids are much more soluble. Citric acid and other acids, however, tend to prevent the precipitation of malic acid by cinchonine.

The vegetable juice is evaporated to dryness in a vacuum, and the residue treated with methylic alcohol. Tartaric acid and potassium hydrogen tartrate, if present, must be removed. The methylic alcohol solution of acids is diluted until it contains about 2·5 per cent. of acid, and solid quinine is added in successive small portions, with continual agitation, until the whole liquid changes to a mass of crystals. The proportion of quinine should not exceed 160—170 parts for every 100 parts of citric acid supposed to be present. After 24 hours the liquid is filtered, and the filtrate is treated in the same way. After removal of the quinine hydrogen citrate, if citric acid is present, cinchonine is added in the same way, in order to precipitate the malic acid. The acids are afterwards readily liberated from the quinine or cinchonine salt. C. H. B.

Presence of a Glucoside of Methylic Salicylate in *Monotropa Hypopithys*, and a Ferment which hydrolyses it. By EMILE E. BOURQUELOT (*Compt. rend.*, 1896, **122**, 1002—1004).—When the stalks of *Monotropa hypopithys* are added to boiling alcohol of 95°, the liquid dissolves a glucoside, which can be isolated in the usual way, and which is probably identical with gaultherin. It is precipitated by ether from its alcoholic solution; its aqueous solution is lævogyrate. If the aqueous solution is boiled with dilute sulphuric acid, it yields methylic salicylate. *Spiræa Ulmaria* and *S. Filipendula*, *Gaultheria procumbens*, *Polygala Senega* and *Betula lenta* contain a ferment which liberates methylic salicylate from the glucoside; it remains in the insoluble matter when parts of these plants are completely exhausted with alcohol of 90°. *Azalea* petals and the root of *Spiræa salicifolia* contain the same ferment, but it is not present in the bark of *Betula alba*. That it is a specific ferment is shown by the fact that it does not affect other glucosides, whilst the glucoside yielding methylic salicylate is not affected by other ferments. It follows that plants which yield methylic salicylate, contain this substance in the form of a glucoside, from which it is liberated by the action of a specific ferment present in the same organs of the plant.

Schneegans has given the name *betulase* to the ferment obtained by Procter from the bark of *Betula lenta*, but the author regards as preferable the name *gaultherase*, which recalls the substance on which the ferment acts (compare Abstr., 1895, ii, 177). C. H. B.

Nitrogen Compounds of Malt and Beer Worts. By E. EHRRICH (*Bied. Centr.*, 1896, **25**, 333—337; from *Bierbrauer*, 1895, 145, 161, and 177; compare Abstr., 1895, ii, 181).—Experiments on the separation of the nitrogenous compounds, showed that lead acetate precipitates more than copper hydroxide, and that phosphotungstic acid precipitates more than lead acetate and tannin together. Tannin precipitates more so-called peptone nitrogen from the filtrate from the albumin precipitate than from the original solutions containing albumin. The method adopted was to precipitate first with lead acetate, and to treat the filtrate (after removal of the lead) with tannin.

In the germination of barley, the proteids become peptonised, the more the nitrogenous compounds are dissolved the further the develop-

ment proceeds (within the ordinary limits of malt production). The most favourable temperature for peptonisation is 50°. Of nitrogen compounds, proteïds have the least nutritive value for yeast.

N. H. J. M.

Composition of the Flower Dust of Sugar Beet. By A. STIFT (*Bied. Centr.*, 1896, **25**, 180—182; from *Oest.-Ung. Zeit. f. Zuckerind. und Landw.*, 1895, **24**, 783—788).—The substance, freed as well as possible from foreign matter, still contained 7·83 per cent. of sand. The following percentage results are calculated on the substance free from sand.

Water.	Protein.	N. as NH ₃ .	Other nitrogenous matter.	Fat.	Starch and dextrin.	Pentosans.	Other N.-free substances.
9·78	15·25	0·41	2·50	3·18	0·80	11·06	23·70
Crude fibre.		Ash.		K ₂ O (in ash).		P ₂ O ₅ (in ash).	
25·45		8·28		5·80		6·65	

The nitrogen as ammonia is probably chiefly in the form of trimethylamine. The substance contains free oxalic acid. Besides cane sugar, the substance contains a second sugar, which reduces Fehling's solution.

N. H. J. M.

Nitrates in Potable Waters. By J. J. THÉOPHILE SCHLOESING (*Compt. rend.*, 1896, **122**, 1030—1038; compare *Abstr.*, 1895, ii, 286).—The author has estimated at various times in the course of 14 months the quantities of calcium and nitric acid in the waters of the Vanne, the Dhuis, and the Avre. In the case of the Vanne and the Dhuis, the variations in the proportions of calcium and nitric acid respectively are in no constant relation to one another, and are not influenced in any definite manner by the volume of water passing down the streams. It would seem, therefore, that the variations are due to geological, rather than to climatic causes. In the case of the Avre, on the other hand, the quantity of calcium and nitric acid present decreases generally when the volume of water in the stream increases, and *vice versa*. Moreover, the proportions of calcium and nitric acid vary, as a rule, in the same direction, and it follows that the water of the Avre is a mixture of true spring water with either surface water or water that has percolated rapidly through soil and rocks in which no formation of nitrates is taking place.

C. H. B.

Analytical Chemistry.

Estimation of Water in Superphosphates. By LEONARD DE KONINGH (*Ned. Tydschr. Pharm., &c.*, 1896, 190—191).—In order to prevent volatilisation of free acid during ignition, in estimating the total amount of water in superphosphates, 5 grams of the sample is mixed with about 1 gram of freshly ignited magnesia, and the

whole is then exposed to a dull red heat. If the sample contains ammonium sulphate, it must be remembered that although the sulphuric acid is completely retained by the magnesia, the ammonia volatilises, and must be allowed for.

This method cannot, of course, be employed if organic substances and nitrates are present.

L. DE K.

Use of Aldehydes containing Ozone for the Detection of extremely small quantities of Iodine in the presence of Chlorine and Bromine. By EUGEN LUDWIG (*Ber.*, 1896, **29**, 1454—1456).—

Aldehydes that have been distilled in a current of air liberate iodine from a solution of an iodide, but have no effect on bromides or chlorides. They do not possess this property after distillation in a current of carbonic anhydride. A very sensitive reagent for iodides can be obtained by leaving 1 c.c. of acetaldehyde for one hour in a 2-litre flask; or by heating benzaldehyde to boiling in a test tube, and making 10 drops of it into an emulsion with 10 c.c. of water. A very small quantity of the reagent is added to the solution of the iodide, and the solution is then shaken with the smallest possible quantity of colourless carbon bisulphide; with 1 part of iodine in 50,000 originally present, a perceptible pink tinge is obtained.

If a solution of potassium iodide is boiled with paraldehyde while a current of air is passed through the mixture, all the iodine is driven over, and potassium acetate remains in the solution.

Since aldehydes can hold ozone in solution for a comparatively long time without becoming oxidised, the author thinks they must form peroxides with it, possibly analogous to the compounds they form with sodium hydrogen sulphite.

C. F. B.

Estimation of Sulphur in Inorganic Sulphides. By PAUL JANNASCH and H. LEHNERT (*Zeit. anorg. Chem.*, 1896, **12**, 129—131; compare Abstr., 1894, ii, 330).—About 0.5—0.75 gram of natural cinnabar is heated in a current of dry oxygen in the apparatus already described by the author, and the evolved sulphurous anhydride collected in a solution of hydrogen peroxide. When the combustion is completed, and the mercury distilled, the apparatus is allowed to cool in a current of gas, and the liquid in the absorption tubes mixed. The sublimed mercury is washed out with hot nitric acid. The solution is evaporated to a small volume, treated with aqua regia to dissolve any mercury remaining, and then evaporated to dryness. The residue is dissolved in water and dilute nitric acid, the sulphuric acid estimated by precipitation with barium chloride, and the mercury weighed as sulphide. When the cinnabar is contaminated with silica, iron, or carbon, this method is especially convenient, as a clear solution is at once obtained.

Commercial crystalline tin sulphide is analysed in a similar manner to the above. The combustion is carried on until the tin dioxide remains unaltered; this is then weighed in the combustion tube.

E. C. R.

Drown's Method of estimating Sulphur in Pig Iron. By GEORGE AUCHY (*J. Amer. Chem. Soc.*, 1896, **18**, 406—411).—The author has slightly modified this process, and operates as follows. 3.4335 grams of the pig iron drillings is introduced into a 16-ounce flask connected with a Troilius' bulb containing 6 c.c. of a 1 per cent. solution of potassium permanganate and 6 c.c. of 20 per cent. aqueous potash. The iron is now dissolved in hot dilute hydrochloric acid, and finally air is drawn through the apparatus by means of a filter pump.

The contents of the bulb are now washed into a small beaker. The iron solution is filtered, and, after being washed, the insoluble residue is rinsed into an evaporating dish. After evaporating to dryness, 30 c.c. of nitrohydrochloric acid is added, and then again evaporated off. The mass is now heated with 10 c.c. of dilute hydrochloric acid, which is then filtered and added to the alkaline permanganate solution, which, of course, contains the greater part of the sulphur. To better reduce the excess of permanganate, a sufficiency of oxalic acid is added, and the liquid is boiled. The sulphuric acid is then precipitated in the usual way with barium chloride. Traces of silica in the potash, or a little undecomposed oxalic acid, do not in the least interfere.

L. DE K.

Estimation of Pyrrhotite in Pyrites. By EDWIN F. CONE (*J. Amer. Chem. Soc.*, 1896, **18**, 404—407).—The author advises examining pyrites for the presence of pyrrhotite (Fe_7S_8), as this is of inferior value to makers of sulphuric acid.

The ground sample is passed through a 60-mesh sieve and 13.74 grams is then weighed and spread out upon a good-sized sheet of glazed paper. By means of a magnet, the pyrrhotite is removed, and by first stroking suddenly the top of the magnet, the mechanically admixed pyrites are separated, and the magnetic substance is then removed by means of the armature and a brush. The process is repeated five or six times, and the magnetic portion is then finely powdered and oxidised by means of nitric and bromohydrochloric acids. From the weight of the barium sulphate, the amount of Fe_7S_8 is calculated.

L. DE K.

New Safety Distillation Tube for Nitrogen Estimations. By CYRIL G. HOPKINS (*J. Amer. Chem. Soc.*, 1896, **18**, 227—228).—This modification of Reitmeir's distillation tube for use in the Kjeldahl process differs from the usual pattern in so far that not only the tube which passes into the distillation flask, but also the tube within the bulb has an opening on the side, and a jet at the end. The vapour passes in through the side openings, and whatever condenses in the top part of the bent tube passes back into the flask through the jets.

All danger of alkaline liquid being mechanically forced into the distillate is thereby avoided.

L. DE K.

Modifications of Pemberton's Volumetric Method of estimating Phosphoric acid in Fertilisers. By F. P. VEITCH (*J. Amer.*

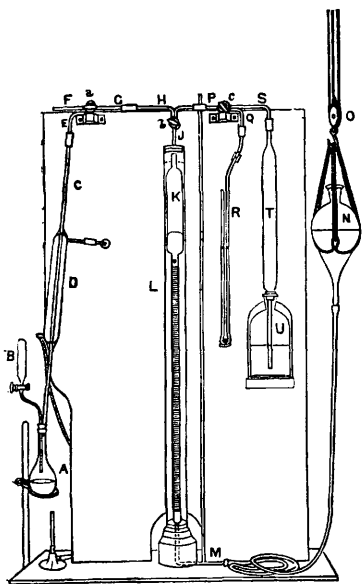
Chem. Soc., 1896, **18**, 389—396).—The author has investigated the various modifications of Pemberton's volumetric molybdate process, and tabulated the results. The final conclusions are: (1) That the best results are obtained by adding 10 per cent. extra nitric acid to the official molybdate solution, and allowing this to act for half an hour at 40—50°. (2) That, although addition of tartaric acid gives good results, it possesses no advantage, and only retards the precipitation of the phosphoric acid.

L. DE K.

[**Analysis of Silicates containing Fluorine.**] By ALFRED REICH (*Monatsh.*, 1896, **17**, 149—171).—See this vol., ii, 531.

Estimation of Carbon in Steel. By ANDREW A. BLAIR (*J. Amer. Chem. Soc.*, 1896, **18**, 223—227).—The 400-c.c. pipette T is connected by means of the stopcocks *b* and *c* with the burette K, and by lowering the mercury reservoir the pipette is filled with aqueous potash of sp. gr. 1.27. The stopcock *c* is closed, the burette

filled with mercury, and *b* then closed. One gram of the steel drillings is introduced into the 200-c.c. flask A, which is then attached to the apparatus. The water is started through the condenser D, and the flask is connected with the burette by means of the stopcock *a*. 15 c.c. of a saturated solution of pure copper sulphate is poured through the funnel tube B into the flask. After it has acted long enough to form a superficial deposit of copper on the metal, 15 c.c. of a 50 per cent. solution of chromic acid and 135 c.c. of the following mixture is added: 35 c.c. of chromic acid solution, 115 c.c. of water, 750 c.c. of sulphuric acid, and 315 c.c. of phosphoric acid of 1.4 sp. gr. The solution in the flask is now raised to the boiling point, and, by means of the reservoir, the mercury in the burette and



the tube M is kept nearly level. The water condensed in the tube C drops back into the flask, and keeps the liquid of the same density, while the cooled gases pass into the burette.

The flask is now allowed to cool for 5 minutes, and is then filled through the tube B with water to the stopcock *a*, thus forcing all the gas into the burette. The cock is then closed, and the burette is connected by means of the stopcocks *b* and *c* with the manometer R containing water; the levels are adjusted accurately, and the reading of the burette is taken. By means of the stopcock *c* the burette is

connected with the pipette T, and by raising and lowering the reservoir N the gas is passed several times backwards and forwards to cause the alkali to absorb all the carbonic anhydride. Another reading is then made, care being taken that the burette contains a few drops of water, and the difference between the two readings represents the volume of the carbonic anhydride, which is then corrected for pressure, temperature, and moisture. The volume of the gas so obtained, multiplied by 0.0019663, gives the weight.

L. DE K.

Rapid and Exact Estimation of Lime in Soils. By A. NANTIER (*Ann. Agron.*, 1896, **22**, 245—246).—The soil (5 grams) is treated with 50 c.c. of acid (100 c.c. of acid = 5 grams of CaCO_3) in a cylindrical glass vessel, and heated rapidly to boiling for 4 or 5 seconds to expel the dissolved carbonic anhydride. Water (50 c.c.) and a few drops of litmus solution are added, and the liquid titrated. When saturated, the liquid becomes reddish-violet, and at the same time the clayey magma is instantly precipitated. The process is very accurate as well as rapid; two operators can easily make 20 determinations in an hour.

N. H. J. M.

Quantitative Analysis by Electrolysis. By MAX HEIDENREICH (*Ber.*, 1896, **29**, 1585—1590).—The author has tested the methods given by Smith for the estimation of various metals by means of electrolysis. The only method, by means of which he has succeeded in getting good results, is that given for copper, whilst in the cases of iron, cadmium, silver, molybdenum, and uranium, the results were unsatisfactory. On the other hand, the separation of lead from mercury, and copper from zinc, in presence of nitric acid, and of silver from copper, silver from zinc, mercury from zinc, and mercury from nickel in presence of potassium cyanide all succeeded well. Silver cannot be separated from lead by the method described by Smith, nor copper from cadmium, although the latter separation can be effected in presence of sulphuric acid.

A. H.

Delicate Form of the Mercury Iodide Reaction. By PAUL JANNASCH (*Zeit. anorg. Chem.*, 1896, **12**, 143—145).—The slightly acid solution of the mercury salt is treated with perfectly clean pieces of copper, and warmed in lukewarm water. The solution is then poured off, the copper washed with cold water, then turned on to filter paper, and carefully pressed until dry. It is then transferred to a test tube, and the neck of the tube drawn out to a capillary. The copper is then heated until the sublimate has collected round the capillary. The bottom of the tube is cut off, and the upper part placed in a cylinder containing a small piece of iodine, when a deposit of red mercuric iodide is obtained. The tube can then be sealed at both ends and kept as a specimen. By this method 0.0005 gram of mercury chloride can be easily detected, but no certain result was obtained with 0.0001 gram. About 0.00001 gram of mercuric chloride can be detected if a copper strip, after treatment with the mercury solution and drying, is placed on a watch glass near to, but not touching, a small piece of iodine, and then covered with another glass for about

10 minutes. Rings of deposited mercuric iodide are formed on the copper, and these when examined under the microscope are seen to consist of dark red quadratic tablets or octahedra, which appear yellow when separated. E. C. R.

Separation of Mercury from other Metals by heating the Sulphides in a Current of Oxygen. By PAUL JANNASCH and H. LEHNERT (*Zeit. anorg. Chem.*, 1896, 12, 132—133).—The same apparatus is employed as for the analysis of sulphides, the three absorption tubes being filled with dilute nitric acid. The separation of mercury and tin is carried out as follows. The metals are precipitated as sulphides, and the precipitate dried at 90°. The precipitate is separated from the filter paper, and the filter paper first burned in the apparatus, the bulk of the precipitate is then added, and the mercury distilled off, whereby white tin oxide remains behind and is weighed in the combustion tube. The mercury is precipitated as sulphide. This method is applicable to the separation of mercury from nearly all organic and inorganic mixtures containing it.

E. C. R.

Separation of Manganese from Copper and Zinc, and of Copper from Zinc and Nickel. By PAUL JANNASCH (*Zeit. anorg. Chem.*, 1896, 12, 134—142; compare *Abstr.*, 1895, ii, 331).—*Separation of Manganese and Zinc.*—The metallic salts (0.4 gram) are dissolved in water (10—18 c.c.) containing a few drops of hydrochloric acid and mixed with acetic acid (15 c.c.). The mixture is then slowly added to a mixture of concentrated ammonia (40—50 c.c.) and 3 per cent. hydrogen peroxide (30—40 c.c.), and heated on the water bath for 10—15 minutes. The precipitate is washed with strong, then with dilute ammonia, and finally with warm water. It is entirely free from zinc. The zinc is estimated in the filtrate by any convenient method.

Separation of Manganese and Copper.—The metallic salts (0.4 gram) are dissolved as above, and the solution gradually added to a mixture of ammonia (60 c.c.) and hydrogen peroxide (50—60 c.c.). The mixture is heated on the water bath for half an hour, filtered, and the precipitate washed with a hot solution of ammonium acetate in concentrated ammonia, and then with ammonia and water. The precipitate is entirely free from copper. The filtrate containing the copper is evaporated to dryness, heated on the air bath, and the copper precipitated either with sodium hydroxide or with sulphurous acid and ammonium thiocyanate.

The precipitate of copper sulphide obtained in an acid solution containing zinc by means of hydrogen sulphide always contains zinc. The author proceeds as follows. In the case of an alloy, about 1 gram is dissolved in nitric acid, the solution evaporated to dryness, and the residue dissolved in dilute nitric acid, and any tin oxide filtered off. The solution is again evaporated to dryness, and the residue dissolved in water and concentrated sulphuric acid (10 c.c.), diluted to 350 c.c., and the copper precipitated at 85—95° by hydrogen sulphide. The copper sulphide, which is quite free from zinc, is converted into oxide by heating in a current of oxygen. The filtrate

containing the zinc is evaporated to 100—150 c.c., and the zinc precipitated with sodium carbonate. Nickel and zinc are separated as follows. The two metals are precipitated together as carbonates, the precipitate dissolved in hydrochloric acid, evaporated to dryness, dissolved in water containing at most 10 drops of hydrochloric acid, and the solution gradually added to a warm solution of pure sodium hydroxide. The mixture is boiled, diluted with water, and the precipitated nickel separated by filtration.

The author discusses the advantages of the alkaline hydrogen peroxide method of separation as compared with the ordinary methods.

E. C. R.

Sarnstrom's Method of estimating Manganese in Iron Ores. By C. T. MIXER and H. W. DuBois (*J. Amer. Chem. Soc.*, 1896, 18, 385—389).—The process is based on the well-known fact that manganese is not precipitated from strongly acid solutions by sodium carbonate, whilst iron is readily thrown down.

The author finds that in the case of ores poor in manganese the process gives excellent results if care is taken to avoid excess of sodium carbonate. The use of the bicarbonate has no practical advantage. After the iron hydroxide has subsided, the liquid is at once warmed to 80°, and titrated with standard permanganate.

For ores rich in manganese, the method is untrustworthy.

L. DE K.

Volumetric Estimation of Manganese. By GEORGE C. STONE (*J. Amer. Chem. Soc.*, 1896, 18, 228—229).—The author thinks that Volhard's method as modified by Auchy (this vol., ii, 339) is unnecessarily complicated, and states that the process gives very accurate results if used as follows.

The quantity of manganese should amount from 0.05—0.15 gram. The sample of iron is dissolved in a suitable acid, but care must be taken to thoroughly oxidise the iron by boiling with nitric acid, or hydrochloric acid and potassium chlorate. After cooling, the solution is mixed with a sufficiency of an emulsion of zinc oxide, and then made up to exactly 500 c.c. When the precipitate has subsided, 100 c.c. of the liquid is put into a basin, diluted to 200 c.c., heated to boiling, and rapidly titrated with standard permanganate while vigorously stirred.

L. DE K.

Separation of Metals in Alkaline Solution by means of Hydrogen Peroxide. XV. By PAUL JANNASCH and H. LEHNERT (*Zeit. anorg. Chem.*, 1896, 12, 124—128).—*Separation of Arsenic and Cobalt.*—A solution of cobalt ammonium sulphate and arsenious acid in nitric acid (2 c.c.) and water (10 c.c.) is gradually added to a solution of pure sodium hydroxide (10 grams) in water (20—25 c.c.), mixed with 3 per cent. hydrogen peroxide (30 c.c.). The mixture is warmed for half an hour on the water bath, diluted with hot water to about 250 c.c., and the precipitate of cobalt hydrated peroxide filtered off, washed with hot water, dried, ignited, and weighed as cobalticobaltous oxide, then reduced to metallic cobalt, and again weighed. The filtrate containing the arsenic is acidified with con-

centrated nitric acid, evaporated to a small volume, mixed with 2 grams of citric acid, and made strongly alkaline with ammonia, when no precipitate should be obtained even on standing. The arsenic is then precipitated with magnesium chloride, and the precipitate washed with dilute ammonia and dried at 90° . The precipitate is separated from the filter paper, the last traces being dissolved off with nitric acid; this solution is evaporated to dryness, and the bulk of the precipitate added and ignited. Arsenic and nickel are separated in a similar manner.

Separation of Manganese and Cobalt.—A solution of manganese and cobalt ammonium sulphates (0.4 to 0.5 gram) in water (10–15 c.c.) containing a few drops of hydrochloric acid is gradually added to a cold solution of sodium hydroxide (6 grams) and pure potassium cyanide (3.5 grams) in water (50 c.c.); a 3–5 per cent. solution of hydrogen peroxide (20–25 c.c.) is then added, and the mixture warmed on the water bath for half an hour. It is then diluted to 250–300 c.c., and the precipitated manganese collected and thoroughly washed with hot water. The precipitate is dissolved in dilute hydrochloric acid and hydrogen peroxide, again precipitated with ammoniacal hydrogen peroxide, collected, ignited, and weighed as Mn_3O_4 . The filtrate containing the cobalt is acidified with concentrated sulphuric acid and evaporated to complete dryness, whereby the cobalt potassium cyanide is converted into sulphate. The residue is dissolved in hot water, and the cobalt precipitated as hydrated peroxide with a solution of sodium hydroxide and hydrogen peroxide, and finally weighed as Co_3O_4 and Co. It is important that the potassium cyanide is pure, as otherwise the precipitates are contaminated with iron; also the solution becomes contaminated with small quantities of silica, which is separated after the evaporation with sulphuric acid. The separation of manganese and nickel is effected in a similar way.

Estimation of Tin.—A solution of the chloride, $SnCl_4(NH_4Cl)_2$ (0.4–0.5 gram), in water (10 c.c.) containing a few drops of hydrochloric acid, is gradually added to a mixture of water (20 c.c.), concentrated nitric acid (10 c.c.), concentrated ammonia (40 c.c.), and hydrogen peroxide (25–30 c.c.). The mixture is heated on the water bath until the precipitate has completely settled; it is then filtered, and the precipitate washed with a 10 per cent. faintly ammoniacal solution of ammonium nitrate, dried at 95° , ignited, and weighed as SnO_2 . The filtrate, when treated with ammonium sulphide and then with hydrochloric acid, gives no precipitate of tin sulphide.

E. C. R.

Detection of Chromates and Arsenites. By N. TARUGI (*Gazzetta*, 1896, 26, i, 220–222).—The author replies to Antony's criticisms (this vol., ii, 390).

W. J. P.

Estimation of the Colours of Natural Waters. By ALLEN HAZEN (*J. Amer. Chem. Soc.*, 1896, 18, 264–275).—The author prepares a comparison liquid by dissolving platinum chloride in water, and adding a sufficiency of cobalt chloride so as to obtain the desired shade of colour.

The colouring matter in the sample is then expressed in degrees of platinum-cobalt. L. DE K.

Detection of Lead and Copper in Potable Waters.—By CORNELIS GULDENSTEEDEN EGELING (*Ned. Tydschr. Pharm., &c.*, 1896, 113—117).—Two hundred and fifty c.c. of the water is acidified with acetic acid, and hydrogen sulphide is passed through it; 0.5 gram of talc which has previously been boiled with dilute nitric acid is then added and the mixture well shaken. The talc as it settles carries down with it even the merest traces of lead or copper sulphide which may have been present. The liquid is poured off, the deposit collected on a cotton-wool filter, and treated with a few c.c. of hot nitric acid. The acid is then evaporated to dryness in a small dish, and the residue tested for copper and lead in the usual way. L. DE K.

Estimation of Small Quantities of Lead in Water. By UBALDO ANTONY and T. BENELLI (*Gazzetta*, 1896, 26, i, 218—220).—In determining small quantities of lead in water, it is advisable to add a considerable proportion of mercuric chloride to a measured volume of the sample, and then treat with excess of hydrogen sulphide; after adding ammonium chloride to ensure the deposition of all the mercuric sulphide, the bulk of the liquid is removed by decantation, the sulphide collected on a filter, dried, and the residue heated either in a current of hydrogen sulphide and weighed as lead sulphide, or in the air, treated with sulphuric acid and weighed as lead sulphate. The addition of the mercuric chloride prevents the lead sulphide assuming the colloidal soluble form; test analyses gave excellent results. W. J. P.

Estimation of Sodium Salicylate in Presence of "Ichthyol." By J. J. HOFMAN (*Ned. Tydschr. Pharm., &c.*, 1895, 103—104).—The sodium salicylate may be separated from the ichthyol by treating the mixture with water, which will leave the greater part of the ichthyol undissolved, and the last traces may be precipitated from the solution by adding an equal bulk of brine. The salicylic acid can then be extracted in the usual manner by acidifying with hydrochloric acid and agitating with ether. L. DE K.

Determination of the Heat of Bromination in Oils. By HARVEY W. WILEY (*J. Amer. Chem. Soc.*, 1896, 18, 378—383).—The process is a modification of the one proposed by Hehner and Mitchell (*Abstr.*, 1895, ii, 427). The bromine is not added undiluted, but is mixed with 4 volumes of either chloroform or, better, carbon tetrachloride.

Ten grams of the oil is dissolved in either of the solvents and diluted to 50 c.c.; 5 c.c. of this solution is mixed in a specially constructed apparatus with 5 c.c. of the bromine solution, and the rise in temperature is observed by means of a delicate thermometer. The author has tabulated the results of experiments with olive oil, calycanthus seed oil, cotton-seed oil, and sunflower seed oil, using both chloroform and carbon tetrachloride. It is advisable to make at least four trials with a sample. L. DE K.

Estimation of the Solid Fat in Artificial Mixtures of Vegetable and Animal Fats and Oils. By J. HOWARD WAINWRIGHT (*J. Amer. Chem. Soc.*, 1896, **18**, 259—264).—The author recommends the following process for the assay of lard compounds (larderine):—150 grams of the sample is placed in a beaker and heated in a boiling water bath until entirely melted. After an hour, the water is allowed to cool to 75—80 F., and the beaker is then put in a moderately warm place for at least 12 hours. This causes the solid fat to crystallise, and after stirring the contents with a glass rod or spatula, 50 grams is weighed out and carefully wrapped in a double thickness of Canton flannel in which it is subjected to pressure in a small screw press, very gradually at first but afterwards as strongly as possible. After the oil has drained off, the contents of the press are removed and the solid cake is weighed.

The results are accurate within one and a half per cent.

L. DE K.

Estimation of added Water in Milk by taking its Freezing Point. By HARTOG J. HAMBURGER (*Ned. Tydschr. Pharm.*, 1896, 209—212).—The author finds that the freezing point of milk varies from 0.574 to 0.556° below zero.

By using Beckmann's freezing apparatus and a thermometer capable of showing hundredths of a degree or less, it becomes possible to detect with certainty the addition of 2 or 3 per cent. of added water. Several samples of milk may be tested in an hour.

The author is fully aware that before the process can be generally introduced, a great many local experiments will have to be made.

L. DE K.

New Method of Testing Quinine. By MELCHIOR KUBLI (*Chem. Centr.*, 1895, ii, 1058—1059; from *Pharm. Zeit. Russ.*, **34**, 593—598, 609—613, 625—628, 641—646).—The author's process for testing commercial quinine sulphate is based on the fact that whilst the sulphates of the inferior alkaloids are more soluble in water than the pure article, the liberated alkaloids behave in an opposite manner.

1.793 gram of the sample dried at 40—50° is placed in a tared flask with 60 c.c. of water and heated to boiling. After five minutes, the amount of water is increased to 62 grams, and the whole is placed for half an hour in water at 20°, well shaken and filtered. 5 c.c. of the filtrate is put into a narrow glass cylinder, three drops (0.8 c.c.) of a solution of sodium carbonate (1—10) is added, and water is now carefully added from a burette, with constant shaking, until the turbidity has completely disappeared. The operation is twice repeated, and, to make sure, the supposed correct amount of water is added at once, and the turbidity should then vanish by rotating three times. If the sample is pure, 10 c.c. of water will be required; but, if not, a larger quantity will be wanted, depending on the quantity and nature of the accompanying alkaloid. The paper will be continued.

L. DE K.

The Testing of Quinine Sulphate. By OSWALD HESSE (*Arch. Pharm.*, 1896, **234**, 195—203).—The author criticises the water test

and the carbonic anhydride test proposed by Kubli (preceding abstract), and points out that, according to his own experiments, neither of these tests gives such accurate results as the official tests, and further, that the results given by the two tests do not agree with one another. A. H.

Acidimetric Estimation of Vegetable Alkaloids. A Study of Indicators. By LYMAN F. KEBLER (*J. Amer. Chem. Soc.*, 1895, **17**, 822—831).—The author has experimented with the following alkaloids: quinine, strychnine, morphine, codeine, and cocaine; also with the crude alkaloids of nux vomica, ipecacuanha, and belladonna.

As regards the indicators, it can be safely concluded that methyl-orange has lost somewhat of its glory. Litmus solution is also quite unsatisfactory for delicate titrations. Hæmatoxylin may claim the best results, whilst Brazil wood comes second, and cochineal third. The author is studying the behaviour of other indicators.

L. DE K.

A Forensic Examination for Strychnine. By LOUIS LEWIN (*Arch. Pharm.*, 1896, **234**, 272—273).—Polemical. A. H.

Detection of the Glucosides of Digitalis and the Products of their Hydrolysis by means of Sulphuric acid containing a Ferric Salt. By HEINRICH KILIANI (*Arch. Pharm.*, 1896, **234**, 273—277).—The reaction which the digitalis glucosides give with sulphuric acid is due to the presence of ferric salts in the latter, and is best obtained by using sulphuric acid, to 100 c.c. of which 1 c.c. of a solution of 5 grams of commercial ferric sulphate in 100 c.c. of water has been added. With this reagent the following reactions may be obtained.

Digitalinum verum is coloured a deep golden yellow, and then forms a red solution, which rapidly changes to a permanent reddish-violet. Digitaligenin gives the same reaction, but with greater intensity. Digitoxin becomes very dark coloured, and then forms a dirty brownish-red solution. Digitoxigenin forms a red solution which is strongly fluorescent. Digitonin and digitogenin, on the other hand, produce no coloration whatever.

Digitoxin may be further identified by the fact that, when it is dissolved in acetic acid containing ferric sulphate (prepared in the same way as the sulphuric acid), and sulphuric acid containing the iron salt then poured into the tube so as to form a layer beneath it, a blue coloration is gradually developed in the acetic acid, whilst the sulphuric acid remains colourless. This coloration in the acetic acid is not produced by any other of these compounds. If digitalinum verum is also present, the sulphuric acid becomes reddish-violet, and the acetic acid indigo-blue. (Compare Keller, *Ber. Pharm. Gesell.*, 1895, Part 11.) The application of this very delicate test has shown that no digitoxin is present in the glucosides extracted from the seeds in the ordinary way.

Digitoxin appears only to exist in one modification, the substance described as α -digitoxin being identical with the β -compound previously described by the author. A. H.

Cubebs and its Adulterants. By KARL PEINEMANN (*Arch. Pharm.*, 1896, **234**, 204—271).—See this vol., i, 494.

F. Hoppe-Seyler's Double Colorimetric Pipette. By GEORG HOPPE-SEYLER (*Zeit. physiol. Chem.*, 1896, **21**, 461—467), and by HUGO WINTERITZ (*ibid.*, 468—480).—The more extensive use of this apparatus is advised. In the first paper, a number of clinical examinations of blood are given. Hoppe-Seyler's method gives higher results than the other well-known colorimetric methods of Gowers and von Fleischl. The second paper shows that the standard used (carbonic oxide hæmoglobin) is permanent for years, and that the colorimetric results are close to those obtained by analysis. Various details in the method of using the instrument are described in full.

W. D. H.

Estimation of Solid Matter in Beef-Tea. By LEONARD DE KONINGH (*Ned. Tydschr. Pharm., &c.*, 1896, 208).—To a weighed quantity of the warm liquid, a weighed quantity of tannin is added, the moisture in which is, of course, known. The gelatin is at once precipitated and the drying therefore proceeds at a rapid rate on the water bath; a short drying at 98—100° will then give a constant weight from which the weight of the dry tannin added must be deducted. The combination of gelatin with tannin is, according to the author, a purely additive product. The residue is, as a rule, more combustible than that obtained in the ordinary way, and leaves a white ash.

L. DE K.

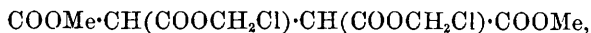
General and Physical Chemistry.

Characterisation of Optically Isomeric Compounds. By PAUL WALDEN (*Ber.*, 1896, **29**, 1692—1707).—According to Pasteur, substances containing an asymmetric carbon atom all crystallise in hemihedral forms. This statement can no longer be maintained, since a very large number of optically isomeric compounds are now known which do not crystallise in hemihedral forms, a large number of these from among the alkaloids, sugars, and terpenes being adduced by the author. Numerous cases, moreover, are now known in which the racemic inactive form of a compound does not differ from the active forms in the same way as racemic acid from dextro- and lævo-tartaric acid, by having a higher melting point and smaller solubility. Thus, many racemic forms have the same melting point, and others again a lower melting point than the optically active isomerides to which they correspond. The author has determined the melting point, density, molecular volume, electrical conductivity (coefficient of affinity), solubility, and crystalline form of a large number of optically active substances and of their racemic isomerides, and has come to the following conclusions. (1) Hemihedry is only a frequent, but not a necessary, accompaniment of optical activity. (2) Both the optically active and racemic forms have the same coefficient of affinity (*K*). (3) The dextro- and lævo-forms of a substance have the same density, solubility, and melting point. (4) The racemic form may have either the same or a lower or a higher melting point than the active isomerides. (5) When the racemic form has a higher melting point it has also a smaller solubility and a smaller molecular volume. (6) Any compound of two oppositely optically active forms of a substance may be considered as a true racemic modification when its crystalline form and density is different from those of the active isomerides. These are usually accompanied by different melting point and solubility.

A. H.

Chlorinated Ethereal Tartrates. By PAUL FREUNDLER (*Bull. Soc. Chim.*, 1895, [3], **13**, 1055—1063).—Le Bel (*ibid.*, **9**, 674) and Walden (*Abstr.*, 1895, i, 450) have shown that optically active substances which contain an atom of chlorine, bromine, or iodine directly united to an asymmetric carbon atom form exceptions to Guye's law of the product of asymmetry. Le Bel has found that the chloracetate of propyl glycol, in which the chlorine is not directly united to an asymmetric carbon atom, does not behave abnormally; the author has undertaken the study of several ethereal salts of tartaric acid, in which the hydroxyls have been etherified by chloracetic acid, in order to see whether they are also normal.

Methylic dichloroacetyl tartrate,



is a syrupy liquid, which distils at 187—190° under a pressure of 14 mm. Its sp. gr. = 1.409 at 18°, and its specific rotatory power $[\alpha]_D = +3.5^\circ$. The corresponding *ethylic* salt boils at 195—197° at 12 mm. pressure, has sp. gr. = 1.311 at 15°, and $[\alpha]_D = +9.4^\circ$. The *propylic* salt boils at 204—205° at 15 mm. pressure; its sp. gr. = 1.245 at 17° and $[\alpha]_D = +11.6^\circ$. The *isobutylic* salt is almost as syrupy as the *methylic*; it distils at 210—215° at 13 mm. pressure; its sp. gr. = 1.195 at 20°, and its specific rotatory power $[\alpha]_D = +13.9^\circ$. These numbers are normal, in so far as the rotatory power increases with an increase in weight of the alkylic group, but they are abnormal in that they are all dextrogyrate, whereas from the law of the product of asymmetry they should be lævogyrate. The author discusses these facts from a theoretical standpoint. Experiments were also made to show the influence of temperature on the rotatory power; in all cases, the rotatory power increases considerably with an increase in temperature.

Different solvents also have an influence on the rotatory powers of these ethereal salts, just as they have on those of the diphenylacetyl-tartrates and the ordinary alkylic tartrates.

	Benzene solution.	Liquid.
Methylic dichloracetyl tartrate	$[\alpha]_D = -1.1^\circ$	+ 3.5°
Ethylic " "	$[\alpha]_D = +10.8$	+ 9.4
Propylic " "	$[\alpha]_D = +9.9$	+11.6
Isobutylic " "	$[\alpha]_D = +8.0$	+13.9

Alcohol, carbon bisulphide, ethylene dibromide, and chloroform have the same effect on the rotatory powers of the dichloracetyl-tartrates as on those of the diphenylacetyl-tartrates.

The molecular weights, as obtained by the cryoscopic method, in benzene and ethylene dibromide solutions, are also abnormal.

J. J. S.

The Action of Nitrous acid in a Grove's Element. By RUDOLPH IHLE (*Chem. Centr.*, 1895, ii, 428; from *Zeits. Electrochem. u. Electrochemie*, 1895, 174—175).—If the nitric acid in a Grove's element is gradually diluted with water, the electromotive force remains nearly constant until the acid contains 38 per cent. nitric acid; on further dilution, the E.M.F. falls from 1.8 to 0.7 volt, and with 28 per cent. of nitric acid has the smaller potential. If, however, potassium nitrite is added to the 28 per cent. acid, the potential rises from 0.7 to 1.8 volt, but falls again to 0.7 as soon as the nitrous acid is destroyed by potassium permanganate, hydrogen peroxide, carbamide, &c. Similarly the potential of a >38 per cent. acid is lowered by the addition of potassium permanganate or of carbamide. It therefore follows that nitrous acid is the real depolariser in a Grove's element (compare this vol., ii, 460).

J. J. S.

A Non-sulphating Phospho-accumulator. By HENRY N. WARREN (*Chem. News*, 1896, 73, 191).—Lead grids of special construction are repeatedly pasted with a composition of litharge and phosphoric and sulphuric acids, and dried for hours at 250° F., until biscuit plates are obtained; these are piled with alternate plates of

amalgamated zinc and insulating carbon blocks in dilute sulphuric acid, with or without 12 per cent. of phosphoric acid, until perfectly reduced; they are then washed and peroxidised, being subsequently soaked in dilute phosphoric acid.

D. A. L.

Electrolysis of Hydrogen Chloride without a Membrane.

By FELIX OETTEL (*Chem. Centr.*, 1895, **76**, 3; from *Zeits. Elektro-techn. u. Elektrochemie*, 1895, 57—58).—If hydrogen chloride is electrolysed without a membrane, the decomposition products are formed in amounts far below the theoretical, as the chlorine which dissolves in the liquid is again converted into hydrogen chloride by the hydrogen at the cathode. The solubility of the chlorine in the solution is reduced by the addition of sodium chloride, magnesium chloride, or magnesium sulphate. The most suitable solution for electrolysis is a concentrated solution of sodium chloride to which sulphuric acid has been added. If the sulphuric acid is added in excess, oxygen is liberated towards the end of the process; if sodium chloride is in excess, sodium hypochlorite is formed, and the evolution of gas ceases when the solution becomes neutral.

H. C.

Calculation of the Conductivity of Mixtures of Electrolytes having a common Ion.

By DOUGLAS MCINTOSH (*Phil. Mag.*, 1896, [5], **41**, 510—516).—MacGregor has developed a method of calculating, from observations of a number of simple solutions of two electrolytes having a common ion, the conductivity of a solution containing both electrolytes, the assumption being made that the ionic velocities of the constituent electrolytes are not changed by the mixing. To test the accuracy of the method, the author has examined mixtures of sodium and potassium chloride solutions, and of solutions of sodium and hydrogen chloride. In the case of mixtures of sodium and potassium chlorides, the differences between the calculated and the observed values increase rapidly as the constituent solutions become more and more nearly saturated, reaching 6·4 per cent. in the case of practically saturated solutions. In the weaker solutions of sodium and hydrogen chloride, the differences between the calculated and observed values are evidently due to accidental errors; in the stronger solutions, the differences become more marked and irregular in magnitude.

The results show that in the case of two electrolytes with a common ion which differ so markedly in ionic velocity from one another as sodium chloride and hydrogen chloride, the dissociation theory enables us to calculate the conductivity of solutions containing both, within the limits of experimental error, up to a mean concentration of about 1 gram.-mol. per litre, and that in the case of solutions of greater mean concentration the calculated value is greater than the observed.

H. C.

Conductivity of Solutions of some Salts in Acetone.

By ST. VON LASZCZYNSKI (*Chem. Centr.*, 1895, **76**, 3; from *Zeits. Elektro-techn. u. Elektrochemie*, 1895, 55—57).—The author has determined the conductivities of solutions of the thiocyanates of potassium, sodium, and ammonium, the chlorides of mercury and potassium, potassium iodide, and silver nitrate in acetone, the conductivity of

which was itself negligible. The values obtained for various dilutions show that solutions in acetone have a smaller conductivity than the corresponding aqueous solutions. The resistances increase with rising dilution in such a manner as to prevent the determination of the limiting value for the molecular conductivity, but the values for μ_{∞} are estimated at 160—170 for potassium iodide and >200 for sodium thiocyanate.

In agreement with Ostwald's view, that the differences in the molecular conductivities depend on the internal friction of the solvents, acetone solutions show higher values for μ_{∞} than aqueous solutions.

H. C.

Electrolysis of Solutions of Salts in Acetone. By ST. VON LASZCZYNSKI (*Chem. Centr.*, 1895, **76**, 3; from *Zeits. Elektrotechn. u. Elektrochemie*, 1895, 57).—A solution of potassium iodide in acetone can be decomposed by the current from six Meidinger cells; iodine appears at the anode and a gas at the cathode. A solution of lithium chloride electrolysed with 100 volts yields lithium at the cathode. The thiocyanates of potassium, sodium, and ammonium give with 7 volts and 0.5 ampère the corresponding amalgam when mercury is used as the cathode; with copper or platinum cathodes a yellow, amorphous deposit is formed, and bubbles of gas appear on both electrodes. From a silver nitrate solution, the metal separates on the cathode.

H. C.

Estimation of the Heat of Combustion of Fuels. By WALTHER HEMPEL (*Zeit. angew. Chem.*, 1896, 350—352).—The material, coal, for instance, is burnt in a calorimetric bomb. The bomb is then heated, and the steam passed into a weighed calcium chloride tube, to which a calcium chloride guard tube has been attached. To collect all the water, the guard tube is connected with a filter pump, and the bomb exhausted. By alternately admitting air and exhausting, the last traces of water may be collected in the weighed tube. The available heating effect is then found by allowing 600 calories for each unit of water.

L. DE K.

Reaction Velocity in the Conversion of Diazoamido- into Amidoazo-derivatives. II. By HEINRICH GOLDSCHMIDT and R. U. REINDERS (*Ber.*, 1896, **29**, 1899—1907; compare this vol., ii, 515).—Benzenediazoamidotoluene is converted by aniline hydrochloride in aniline solution into amidoazobenzene, and not into tolueneazoaniline. The conversion of paradiazoamidotoluene into amidoazotoluene in paratoluidine solution by paratoluidine hydrochloride proceeds in the normal manner, the rate of change being proportional to the concentration of the hydrochloride of the base.

Experiments with the hydrochloride, trichloracetate, and dichloracetate of aniline and diazoamidobenzene show that the rate of change is roughly proportional to the rate of inversion of sugar produced by the corresponding acids in aqueous solution. The authors therefore consider it probable that the effective agent in the production of the change is the hydrogen ion of the acid combined with the anilide, and that aniline hydrochloride is decomposed in aniline solution into the acid and the base. This view is

supported by the fact that the solubility of hydrogen chloride in aniline is raised by the addition of indifferent compounds to the aniline in the same way as that of hydrated salts in water. The same thing holds for solutions of picric acid in toluidine. A further confirmation of this view is that diazoamidobenzene is converted into amidoazobenzene in dimethylaniline solution by weak acids, such as benzoic acid, which crystallise out in the free state from solution in dimethylaniline. A. H.

Note.—The authors do not discuss the possibility that the change may be brought about by the "ammonium ion" $C_6H_5\cdot NH_3$, of the dissociated salt.—A. H.

Etherification of Substituted Acetic acids. By D. M. LIGHTY (*Amer. Chem. J.*, 1896, **18**, 590—600; compare Abstr., 1895, ii, 159). A temperature of 80° was deemed more suitable than that previously used (154° ; *loc. cit.*) for the determination of etherification values, and for the sake of better comparison than could be obtained by the former method, the estimations were made at much shorter intervals, namely, 1, 3, 5, 10, &c., minutes, instead of 1, 2, 4, 6, &c., hours. The following results were obtained.

	Initial rate (one minute).	Limit of etherification.
Chloracetic acid	1.78 per cent.	68.65 per cent.
Dichloracetic acid	4.56 "	71.22 "
Trichloracetic acid	9.99 "	74.00 "

The limit of etherification of acetic acid is 66.57 per cent. It will be seen that the influence of chlorine is much greater on the rate of etherification than on the limit. A. G. B.

Apparatus for Distillation in a Vacuum. By PAUL C. FREER (*Amer. Chem. J.*, 1896, **18**, 585—586).—An improved receiver for distillation in a vacuum in which the receiving tubes are contained in a bell-mouthed cylinder closed at the shoulder by a gutta-percha plug, through which pass the condensing tube, the rotatory shaft which carries the receiving tubes, and the tube connected with the vacuum pump; the bell mouth of the cylinder contains mercury, which forms an air-tight layer over the gutta-percha plug. A. G. B.

Apparatus for the Electrolysis of Hydrochloric acid. By GEORGE O. HIGLEY and B. J. HOWARD (*Amer. Chem. J.*, 1896, **18**, 584—585).—An improved apparatus for demonstrating the volumetric composition of hydrochloric acid by electrolysis, in which the liberated gases traverse but a small layer of liquid, and are collected and measured in tubes distinct from those containing the electrodes.

A. G. B.

Lecture Experiment: Electrolysis of Hydrochloric acid. By J. M. PICKEL (*Ber.*, 1896, **29**, 1942—1945; compare L. MEYER, Abstr., 1894, ii, 232).—The production of less chlorine than hydrogen when hydrochloric acid is electrolysed in a lecture experiment, has been

already explained, and to some extent obviated by L. Meyer (*loc. cit.*). The author describes a form of apparatus in which the electrolyte is the only liquid through which the escaping chlorine must travel; the gas itself is not measured, but is caused to displace its own volume of air, which can then be estimated. By means of the new apparatus, a lecture experiment yields results which approximate closely to those required by theory.

M. O. F.

Apparatus for demonstrating that two Volumes of Hydrogen and one Volume of Oxygen form two Volumes of Water Vapour. By PAUL C. FREER (*Amer. Chem. J.*, 1896, **18**, 586—587). —An improved tube for demonstrating the volumetric composition of steam in which the eudiometer tube has a stopcock at its upper end, and is attached to a flexible tube from a mercury reservoir at its lower end.

A. G. B.

Volumetric Composition of Ammonium Chloride. By DOUGLAS JOHN CARNEGIE and H. WALES (*Chem. News*, 1896, **73**, 206). —A tube is used, open below, stoppered at the top, and divided by a stopcock into two portions, so that the lower portion down to a mark is of twice the capacity of the upper portion. The upper portion is filled with dry hydrogen chloride, the lower portion with kerosene, saturated with dry ammonia; it is inverted in a glass trough containing the same liquid, and then filled down to the mark with dry ammonia; on opening the stopcock combination ensues, and in course of time the lower portion of the tube becomes filled with the kerosene, whilst the upper portion contains the ammonium chloride and the excess of ammonia, 1 vol.

D. A. L.

Inorganic Chemistry.

Ozone. By CARL ENGLER and W. WILD (*Ber.*, 1896, **29**, 1929—1940).—Various hypotheses have been advanced to account for the production of a mist when ozone is led through a reducing agent and brought in contact with water vapour. It has, for instance, been stated that oxygen, when electrified, yields two modifications, ozone and antozone, the latter being characterised by producing the mist in question on removal of the former; this view was shown to be incorrect by Engler and Nasse, who pointed out that the hypothetical antozone was only formed on decomposing the ozone, at the same time suggesting that the fog producer is not a modification of oxygen, but the vapour of hydrogen peroxide. The present investigation indicates that this conclusion in turn has no experimental foundation, having established the fact that the fog under discussion consists of definite chemical compounds, usually solids, produced by the oxidation of a deozoneiser. These substances are finely divided, or in some cases develop mist, owing to their hygroscopic

properties; they may be acidic, neutral, or even basic, and escape absorption by water or alkalis entirely from mechanical causes.

The production of mist is found to depend on the presence in the deozoneiser of a gaseous, or readily volatile substance, capable of yielding a solid, or hygroscopic, product of oxidation. Thus the phenomenon is observed in the case of solutions containing iodine, or from which iodine is liberated under the influence of ozone, this being oxidised to iodic acid; sulphurous acid yields sulphuric acid, whilst ammonia and solutions of ammonium salts give rise to ammonium nitrate. Liquids containing hydrogen sulphide owe their fog-producing character to the liberation of sulphur.

For the experimental evidence on which these conclusions are based, together with the explanation of minor points in connection with this phenomenon, reference must be made to the original paper.

M. O. F.

Oxidation of Sodium Sulphide and Hydrosulphide to Sulphate by Electrolysis. By FRANK W. DURKEE (*Amer. Chem. J.*, 1896, 18, 525—536).—During the electrolysis of a dilute solution of sodium sulphide (containing about 3·4 grams of sodium in 400 c.c.) by a current of about 3 ampères (voltage not given), hydrogen was evolved at the cathode, and the liquid became yellow, at first around the cathode and ultimately throughout; light yellow sulphur then appeared on the anode, but scaled off again, and in greater part dissolved; fine white sulphur next separated near the surface of the liquid about the anode, but dissolved as it sank through the solution until a certain stage of the electrolysis, when the yellow colour of the liquid disappeared, and the white sulphur settled in the beaker; subsequently more oxygen escaped than at any previous stage. Experiments, in which sodium thiosulphate solution and sodium polysulphide solution respectively were electrolysed, showed that the separation of white sulphur described above connotes the oxidation of thiosulphate, whilst the separation of yellow sulphur is incidental to the presence of polysulphide. These facts, in conjunction with the analytical data given in the paper, indicate that the course of oxidation of sodium sulphide by electrolysis is similar to that of its oxidation by air, which has been elucidated by Lunge; the sulphide is first oxidised to hydroxide and thiosulphate, the latter passing to sulphate with separation of sulphur; this sulphur dissolves in unaltered sulphide to form polysulphides, which are oxidised to thiosulphate with separation of sulphur. Thus during the electrolysis, sulphides disappear first, then the hydroxide, and finally the thiosulphate, the sulphate being virtually the end product. It was noticed that when attempts were made to electrolyse sodium sulphide solution with an alternating current, the platinum electrodes dissolved, whereas no such dissolution was noticed in the case of the direct current electrolysis.

A. G. B.

Volatility of Red Phosphorus. By HENRYK ARCTOWSKI (*Zeits. anorg. Chem.*, 1896, 12, 225—228).—When commercial red phosphorus is heated for 10 days at a temperature of 108° in an apparatus so arranged that the volatile products are condensed on a cold tube,

crystal skeletons are obtained, consisting of nodules of yellow phosphorus, containing small pieces of the red modification. Red phosphorus, previously washed with carbon bisulphide, when heated at 100° for 48 hours in a vacuum of 14–16 mm., volatilises, and forms carmine-red, transparent, microscopic crystals, which are not, however, well formed.

E. C. R.

Action of Hydrogen Iodide and of Phosphonium Iodide on Thiophosphoryl Chloride. By ADOLPHE BESSON (*Compt. rend.*, 1896, **122**, 1200–1202).—Hydrogen iodide dissolves without change in thiophosphoryl chloride cooled in a mixture of ice and salt, but at 0° hydrogen chloride and hydrogen sulphide are given off, and the liquid contains free iodine and phosphorus triiodide, the action being analogous to that of hydrogen iodide on phosphorus oxychloride (this vol., ii, 472).

In sealed tubes at temperatures above 0° , the reaction is more complex, and the products depend on the temperature. In all cases iodine is liberated, hydrogen chloride and sulphide are given off, and the liquid contains phosphorus triiodide and a mixture of phosphorus trisulphide and pentasulphide in varying proportions, together with small quantities of the thioiodide, P_2SI_2 , an orange solid, which melts at about 75° , and is very soluble in carbon bisulphide. The thioiodide does not sublime in a vacuum, decomposes when exposed to air, and readily when heated. In order that it may be formed in appreciable quantity, the solution of hydrogen iodide in the thiophosphoryl chloride must not be heated above 30 – 40° .

Phosphorus trisulphide is formed in very small quantity only by the action of hydrogen sulphide on phosphorus triiodide. It is, however, formed by the action of phosphonium iodide on thiophosphoryl chloride, and the author considers that an unstable thiophosphoryl iodide, PSI_3 , is first formed, and subsequently decomposes into the trisulphide, triiodide, and free iodine.

C. H. B.

Crystalline Silicon. By GUILLAME J. L. DE CHALMOT (*Amer. Chem. J.*, 1896, **18**, 536–540).—The author finds that the mixture of silica, lime, and carbon, which he heats in an electric furnace for the purpose of obtaining calcium silicide and crystalline silicon (this vol., ii, 473), yields very little of the former product unless it contains iron. The mixture of silicide and silicon is specifically lighter than the slag, and, moreover, tends to move towards the cathode; hence separation is aided if the furnace be upright and the cathode the upper electrode. Mixtures containing Mn_3O_4 , quartz, charcoal, and lime, when heated in the electric furnace, yielded mixtures consisting mainly of a manganese silicide, probably $MnSi_2$, and crystalline silicon, which were separated by treatment with hydrofluoric acid and hydrochloric acid; the yield of silicon was 33 per cent., and it contained 97.77 per cent. of silicon, and was free from manganese.

A. G. B.

Action of Metals on Nitric acid. By GEORGE O. HIGLEY and W. E. DAVIS (*Amer. Chem. J.*, 1896, **18**, 587–590; compare Abstr.,

1895, i, 164).—Figures and curves are given illustrative of the action of nitric acid of diverse strengths (sp. gr. 1.05—1.40) on silver foil. Neither nitrogen nor nitrous oxide was produced in any of the experiments; nitric peroxide is the principal reduction product with concentrated acid, accounting for over 70 per cent. of the metal dissolved; the decrease of this gas and the complementary increase of nitric oxide as the acid is diluted is due to the decomposition of the nitric peroxide into nitric acid and nitric oxide by water.

A. G. B.

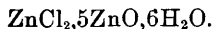
Silver Peroxynitrate. By EDUARD MULDER and J. HERINGA (*Rec. Trav. Chim.*, 1896, 15, 1—51).—The authors have investigated Ritter's black compound formed, under certain circumstances, in a silver voltameter when an aqueous solution of silver nitrate is electrolysed (compare also *Ann. Chim. Phys.*, 1880, [5], 21, 174, and *Compt. rend.*, 1882, 94, 573, and 653). The apparatus used consisted of a platinum reservoir of about 1 litre capacity, which served as the cathode, and which was nearly filled with a silver nitrate solution; the anode was formed of platinum wire, and placed just under it was a small glass vessel, which served to collect the black compound as it was formed. Two series of experiments were made, one series in which the solution was kept neutral by means of silver carbonate, and the other series in which the solution was not neutralised. Solutions of different strengths were used, the strongest contained 1000 grams silver nitrate in 1 litre of solution; weaker solutions were also tried, and experiments are being carried on with still weaker. Minute details as to the methods of analysis adopted are given; in most cases two or three different methods were tried. The black compound is liable to undergo spontaneous decomposition, oxygen being eliminated at the ordinary temperature and also on slightly warming; this oxygen the authors term the *oxygen excess*. Besides determining this oxygen excess, the authors have also estimated, in each case, the amount of silver nitrate and silver oxide, Ag_2O , contained in the black compound. The quantity of the compound deposited on the anode has also been determined, together with the amount of silver deposited on the cathode. The analysis of the black compound, obtained from very concentrated solutions, points to the composition $3\text{Ag}_2\text{O}, 5\text{O}, \text{AgNO}_3$, perhaps $2\text{Ag}_2\text{O}_4, \text{AgNO}_3$, or $3\text{Ag}_2\text{O}_2, \text{AgNO}_5$.

There appears to exist a maximum of concentration with which a maximum of formation of the black compound coincides; the latter dissolves in nitric acid, yielding a brown solution. This accounts for the silver nitrate solution turning brown when electrolysed, as nitric acid is then set free. The compound is decomposed by water, but only very slowly, and the decomposition depends on the quantities and relationships of other substances present, for example, nitric acid, silver nitrate, &c.

J. J. S.

Decomposition of Zinc Chloride by Water. By F. LOUIS PERROT (*Bull. Soc. Chim.*, 1895, 13, 975—979).—The oxychloride of zinc, which is obtained on diluting a syrupy solution of zinc chloride

with water, has been shown by André (*Ann. Chim. Phys.*, 1885, [6], 3, 95) to have the composition $\text{ZnCl}_2, 5\text{ZnO}, 8\text{H}_2\text{O}$. The author finds that a precipitate is formed when pieces of pure anhydrous zinc chloride are dissolved in excess of water. This precipitate, when dried at 38° over sulphuric acid, has the composition



The difference between the two compounds is, beyond doubt, due to the different methods of drying.

The author has followed this decomposition quantitatively by estimating the amount of oxychloride formed on dissolving the same quantity of zinc chloride in different quantities of water.

The point of equilibrium appears to be reached when 75 molecular proportions of water are used to each molecular proportion of zinc chloride.

J. J. S.

Preparation of pure Zinc Sulphate from Crude Zinc Vitriol.

By J. KNOBLOCH (*Chem. Centr.*, 1895, 11, 435—436; from *Pharm. Zeit.*, 40, 472—473).—The boiling zinc vitriol solution is treated with sufficient zinc fluoride to precipitate all the calcium and magnesium, but an excess should not be used, or if used should be removed by gypsum. Zinc oxide, mixed with water, is then added, the whole is left for a day, with occasional stirring, then filtered, acidified with a little sulphuric acid, and the filtrate evaporated till it begins to crystallise. If the crystals contain chlorine, it is necessary to recrystallise from water.

J. J. S.

Cupric Sulphide. By JOHN B. COPPOCK (*Chem. News*, 1896, 73, 262).—Copper sulphide precipitated in the presence of free acid is found to be contaminated with free sulphur; when, however, solution of copper sulphate in known excess is added to a solution containing a known quantity of hydrogen sulphide, the weight of precipitate obtained indicates the composition CuS ; the existence of a sulphide of this composition has been disputed.

D. A. L.

Colloid Compounds of Rare Metals. By MARC DELAFONTAINE (*Chem. News*, 1896, 73, 284).—When ammonia, in amount just sufficient to give a faint odour and turn blue litmus red, is added to a moderately strong solution of yttrium acetate, a slightly opalescent solution is obtained, which becomes turbid, but forms no precipitate; on boiling, however, it deposits a jelly, which redissolves on cooling, provided the boiling is not prolonged; when dialysed, ammonium acetate and part of the earthy acetate pass through the membrane. By leaving yttria many days in a clear solution of normal acetate and stirring frequently, the earth dissolves, and the same colloid compound is obtained in a transparent, opaline, slightly fluorescent solution, depositing no sediment, having a strongly astringent, slightly sweetish taste, and turning red litmus blue. It is not very stable, especially after long dialysis; it coagulates on boiling, or even at about 60° , and when evaporated at the lowest possible temperature, it leaves a varnish that does not "integrally"

redissolve in cold water; when calcined, it chars to some extent, owing to retention of acetic acid. Didymium, lanthanum, and erbium acetates give similar compounds, the didymium colloidal solution being less stable than that of yttrium. D. A. L.

Action of Water, &c., on Aluminium. By EDUARD DONATH (*Chem. Centr.*, 1895, **11**, 589; from *Zeits. angew. Chem.*, 1895, 141).—Hard aluminium foil is not attacked by boiled water which is free from air, whereas ordinary water acts on it appreciably. Calcium sulphate solution has no action, but solutions of chlorides, and especially of nitrates, dissolve the foil readily. Fats, fatty acids, and fused anhydrous phenol are all without action, but a 10 per cent. boiling solution of phenol forms yellow spots, and part of the aluminium goes into solution. The author attributes this more to the action of the air than to that of the phenol. J. J. S.

Chemistry of Iron. By EDUARD DONATH (*Chem. Centr.*, 1895, **1**, 1010—1011; from *Oesterr. Zeits. Berg-Hütt.*, **43**, 147—152).—The author has repeated Bourgeois and Schützenberger's experiments (this Journal, 1875, 788). He has treated large lumps of spiegeleisen with sodium-copper chloride solution, then with a ferric chloride solution previously acidified with hydrochloric acid, and finally with very dilute hydrochloric acid; a brown residue was obtained, which, on treatment with nitric acid, yielded nitrographitoic acid to which Bourgeois and Schützenberger have ascribed the formula $C_{22}H_{17}(NO_2)O_{11}$. It is readily soluble in water, yielding a deep black solution; the ammonium salt yields even deeper coloured solutions. The barium and lead salts have also been prepared; both are insoluble in water, and could not be obtained in a crystalline form.

The author has also repeated De Koninck's experiments (*Chem. Centr.*, 1891, i, 438), and has treated spiegeleisen with warm, dilute, sulphuric acid (1 : 5); he finds that a fatty organic residue remains, and that this dissolves in ether, yielding a deep yellow solution. It follows that, on treatment with acids, the combined carbon in iron yields, besides volatile products, non-volatile organic compounds, part of which are soluble in water and part in ether. This points to the conclusion that the carbon exists in iron in the form of different carbides of high molecular weight. J. J. S.

Molybdenite and the Preparation of Molybdenum. By M. GUICHARD (*Compt. rend.*, 1896, **122**, 1270—1272).—Molybdenite from Sweden was found to contain small quantities of iron and silica with traces of manganese and minute traces of selenium.

When heated in a carbon tube in the electric furnace with a current of 350 amperes and 60 volts, sulphur and sulphurous anhydride are given off. With 900—950 ampères and 50 to 55 volts, molybdenite fuses in two minutes, and decomposes with liberation of carbon bisulphide, sulphur, and a little selenious anhydride. After three minutes, decomposition is almost complete, and after five minutes the molybdenum is saturated with carbon, and the whole of the sulphur

is expelled. The product contains about 91 per cent. of molybdenum, 2 per cent. of iron, and 7 per cent. of carbon. C. H. B.

Niobium. By AKSEL LARSSON (*Zeits. anorg. Chem.*, 1896, **12**, 188—207).—In order to obtain crystalline niobates, the author fuses the amorphous niobates with their respective chlorides, and also according to Ebelmen's method with boric acid in a porcelain furnace. The crystalline niobates obtained by the dry method are not attacked by cold or boiling dilute acids, and they are only decomposed by concentrated sulphuric acid at its boiling point. They are decomposed with difficulty by means of fused potassium hydrogen sulphate, and a complete decomposition is effected only at a red heat. They are partially decomposed by a mixture of hydrofluoric acid and sulphuric acid at the temperature of the water bath. The analysis is effected by decomposing the salts with potassium hydrogen sulphate. The melt is lixiviated with water, and the niobic acid separated by filtration, and washed with a dilute solution of ammonium nitrate or carbonate. The niobic acid is then ignited, and again fused with potassium hydrogen sulphate, this operation being repeated, if necessary, until the salt is completely decomposed. The niobic acid is finally heated over the blowpipe and weighed.

Magnesium niobate, $4\text{MgO} \cdot \text{Nb}_2\text{O}_5$, is obtained by adding magnesium chloride to a solution of potassium niobate, and fusing the precipitate with anhydrous magnesium chloride. By lixiviating the melt with water and hydrochloric acid, the crystalline salt is obtained. It crystallises in tablets and prisms belonging to the hexagonal system: sp. gr. = 4.43.

Magnesium niobate, $\text{MgO} \cdot \text{Nb}_2\text{O}_5$, is obtained by fusing the precipitated salt with boric acid, and lixiviating the melt with water. It forms small prismatic crystals, showing a stronger double refraction than calcium metaniobate.

Calcium niobate, $2\text{CaO} \cdot \text{Nb}_2\text{O}_5$, is obtained by precipitating a solution of calcium niobate with calcium chloride, and fusing the precipitate with anhydrous calcium chloride. By lixiviating the melt with water, the salt is obtained in thick needles, mixed with slender needles of niobic acid.

Calcium niobate, $\text{CaO} \cdot \text{Nb}_2\text{O}_5$, obtained by fusing the precipitated salt with boric acid and lixiviation with dilute hydrochloric acid, crystallises in needles and short prisms which probably belong to the rhombic system: sp. gr. = 4.12.

Copper niobate, $\text{CuO} \cdot \text{Nb}_2\text{O}_5$, obtained by fusing the precipitated salt with boric acid and lixiviating with dilute hydrochloric acid, forms crystalline aggregates having lustrous faces: sp. gr. = 5.60.

Zinc niobate, $\text{ZnO} \cdot \text{Nb}_2\text{O}_5$, sp. gr. = 5.69, forms brown crystalline aggregates which have a colour and lustre similar to zinc blende.

Cadmium niobate, $\text{CdO} \cdot \text{Nb}_2\text{O}_5$, sp. gr. = 5.93, forms a yellowish-brown crystalline powder.

Cobalt niobate, $\text{CoO} \cdot \text{Nb}_2\text{O}_5$, sp. gr. = 5.56, is obtained as a dark blue crystalline powder, having a faint double refraction.

Yttrium niobate, $\text{Y}_2\text{O}_3 \cdot \text{Nb}_2\text{O}_5$, sp. gr. = 5.52, is obtained by fusing the precipitated salt with yttrium chloride. Yttrium niobate,

$\text{Y}_2\text{O}_3, 3\text{Nb}_2\text{O}_5$, sp. gr. = 4.83, is obtained by fusing the precipitated salt with boric acid. It crystallises in slender needles.

Manganese niobate, $3\text{MnO}, 5\text{Nb}_2\text{O}_5$, sp. gr. = 4.97, is a dirty green crystalline powder consisting of prismatic needles and tablets.

Thorium niobate, $5\text{ThO}_2, 16\text{Nb}_2\text{O}_5$, sp. gr. 5.21, is obtained by fusing the precipitated salt with boric acid. It crystallises in prismatic needles.

Zirconium niobate, $\text{ZrO}_2, 5\text{Nb}_2\text{O}_5$, sp. gr. = 5.14, crystallises in slender truncated needles.

When lanthanum, barium, and strontium niobates, obtained by precipitating potassium niobate with the respective chlorides are melted with the anhydrous chlorides, niobic acid is obtained. A crystalline *lanthanum niobate*, containing 78.5—78.8 per cent. Nb_2O_5 and 18.5—20 per cent. La_2O_3 , is obtained by fusing the precipitated salt with boric acid. The author has also obtained crystalline salts from precipitated nickel, beryllium, barium, strontium, and uranium niobates by fusing them with boric acid.

When niobic acid is heated with carbon in an electric arc, a metallic crystalline regulus is obtained. 0.1370 gram of this product, when heated in a current of oxygen, gave 0.1745 gram Nb_2O_5 and CO_2 = 0.0068 gram C.
E. C. R.

Preparation of Sodium Thioantimonate (Schlippe's Salt).

By LÉON PRUNIER (*J. Pharm.*, 1896, [6], 3, 289—290.—Purified antimony trisulphide is melted with a third of its weight of sulphur, and is thus converted into the pentasulphide; this is pulverised and introduced into a flask fitted with a cork and glass tube, and is then treated with a boiling solution of sodium sulphide (one part of crystalline sulphide to 15 of water). On cooling, the liquid is filtered, and the filtrate evaporated to a small bulk, when Schlippe's salt, $\text{Sb}_2\text{S}_5, 3\text{Na}_2\text{S} + 18\text{H}_2\text{O}$, separates in the crystalline form.

J. J. S.

Chemistry of the Cyanide Process for dissolving Gold. By GEORGE A. GOYDER (*Chem. News*, 1896, 73, 272—273; compare this vol., ii, 28).—Hydrogen sulphide, or an alkaline sulphide, is found to interrupt the solvent action of potassium cyanide solution on gold, which, however, can be restored by means of mercuric oxide or chloride.

Experiments with portions of the same cyanide solutions, show that when exposed to zinc alone more gold is deposited than when exposed to both zinc and iron in contact, and, moreover, a loss of soluble cyanide occurs in the latter, but not in the former case.

With regard to the so-called "selective" action of dilute cyanide solutions for gold, it is pointed out that the dissolution of copper in potassium cyanide is a function of concentration, whilst the dissolving of gold in potassium cyanide depends on the proportion of oxygen present, which is a function of dilution, consequently more gold than copper is dissolved by the more dilute solutions; moreover, gold is dissolved by the double cyanides, and is apparently not precipitated except by the interaction of a free metal.
D. A. L.

Double Salts of Ruthenium and Silver. By L. BRIZARD (*Bull. Soc. Chim.*, 1895, [3], **13**, 1092—1093).—The double chloride of nitroso-ruthenium and potassium, when treated with an ammoniacal solution of silver chloride, gives at once a rose-coloured crystalline precipitate of a compound, $\text{RuNOCl}_3, 2\text{AgCl}, \text{NH}_3$. This compound is decomposed by water, giving a precipitate of silver chloride; it is sparingly soluble in ammonia, readily in sodium thiosulphate or potassium cyanide solution. When heated it first melts, and then decomposes, yielding fumes of ammonium chloride. The corresponding bromine derivative, $\text{RuNOBr}_3, 2\text{AgBr}, \text{NH}_3$, which may be prepared in a similar manner, forms clear, green crystals, and in its properties resembles the above compound. J. J. S.

Mineralogical Chemistry.

Classification of Minerals according to the Periodic System of the Elements. By E. SCHULZE (Marburg) (*Zeits. Kryst. Min.*, 1896, **26**, 189—191).—In a tabular arrangement with five classes, namely, elements, thiodids, haloids, oxygen salts, and sulpho-salts, the groups are arranged according to the valency of the acid radicle.

L. J. S.

Arsenic in Coal. By W. M. DOHERTY (*Chem. News*, 1896, **73**, 191—192).—Various New South Wales coals were examined for arsenic, but none was detected. Lead and copper were found in two instances.

D. A. L.

Acanthite from Colorado. By ALBERT H. CHESTER (*Zeits. Kryst. Min.*, 1896, **26**, 526; from *School of Mines Quart.*, 1894, **15**, 103—104).—Acanthite occurs at the Enterprise mine, near Rico, as iron-black crystals of orthorhombic habit, and showing striated prisms with a basal plane or with acute terminations. The material is silver sulphide, with 12.58 per cent. of sulphur and traces of iron and copper. With the crystals is a massive silver sulphide, which is considered to be acanthite rather than argentite.

L. J. S.

Pseudomorphs of Copper Oxides and Sulphides. By PAVEL V. VON JEREMÉEFF (*Zeits. Kryst. Min.*, 1896, **26**, 333—334; from *Verh. k. russ. min. Ges.*, 1894, **31**, 398—400).—The following pseudomorphs from various Russian localities are described. Kaolin (steinmark) after malachite. Tenorite after cuprite and chalcotrichite. Pyrrhotite after cuprite; here the cuprite has first been oxidised to tenorite, and this afterwards replaced by pyrrhotite. Copper pyrites after copper glance. Cuprite after malachite.

L. J. S.

Pickeringite from the River Mana District. By WALDIMIR ALEXEEFF (*Zeits. Kryst. Min.*, 1896, **26**, 336; from *Verh. k. russ. min. Ges.*, 1894, **31**, 350—351).—Besides the normal white mineral of this

locality, a yellow variety of pickeringite is found, in which most of the alumina is replaced by ferric oxide, and the magnesia by ferrous oxide. L. J. S.

Analyses of Samarskite, Pyrochlore, Tantalite, and Niobite [Columbite]. By K. VON CHRUSTSCHOFF (*Zeits. Kryst. Min.*, 1896, **26**, 335—336; from *Verh. k. russ. min. Ges.*, 1894, **31**, 415—417).—
I. Samarskite from the Urals. II. Pyrochlore from the Urals.

	Ta ₂ O ₅ .	Nb ₂ O ₅ .	TiO ₂ .	SiO ₂ .	GeO ₂ .	SnO ₂ .	ZrO ₂ .	ThO ₂ .	UO ₃ .	WO ₃ .
I.	11.18	32.02	0.68	0.12	0.07	0.79	1.03	1.73	11.23	1.41
II.	—	56.01	8.32	—	trace	—	trace	4.28	—	—

	Ce ₂ O ₃ .	Di ₂ O ₃ .	La ₂ O ₃ .	Yt ₂ O ₃ .	Er ₂ O ₃ .	Fe ₂ O ₃ .	Al ₂ O ₃ .	FeO.	MnO.	CaO.
I.	0.25	1.56	0.37	7.83	13.37*	2.13	0.19	11.15	0.69	0.51
II.	2.16	1.94	1.23	0.56	—	—	—	2.52	—	14.05

	MgO.	PbO.	ZrO.	UO.	K ₂ O.	Na ₂ O.	H ₂ O.	F.	Total.	Sp. gr.
I.	0.41	0.15	6.17	—	0.21	0.28	1.22	—	100.77	5.899
II.	—	—	—	2.63	0.87	3.35	—	2.77	100.69	4.354

III. Tantalite from Finland. IV. Columbite from N. Carolina.

	Ta ₂ O ₅ .	Nb ₂ O ₅ .	TiO ₂ .	GeO ₂ .	SnO ₂ .	WO ₃ .	FeO.	MnO.	Total.	Sp. gr.
III.	23.97	49.56	0.77	0.02	2.17	0.96	9.86	11.98	99.29	6.211
IV.	68.15	11.15	trace	0.03	1.65	1.29	15.32	2.61	100.69	7.314

L. J. S.

Chemical Composition and Optical Characters of Russian Albite. By SERGEI F. GLINKA (*Zeits. Kryst. Min.*, 1896, **26**, 509—515; from *Verh. k. russ. min. Ges.*, 1894, **31**, 1—154).—Analyses and the optical constants (extinction and double refraction in plates cut in certain directions, and orientation of the acute bisectrix) are given of albite from various Russian localities. I. Crystals from Slatoust; sp. gr. 2.62 to 2.626. II. Crystals, enclosing rutile, from Kyschtym; here about 0.5 per cent. TiO₂ is included in the SiO₂ and Al₂O₃ in the analysis. III. From Kiräbinsk. IV. From the Melnikow mine, S. Urals. In these cases the calcium, &c., is considered to be present in enclosures, and from the observations the following optical constants are deduced for pure albite. Optic axial angle = 73—74°, $\gamma - \alpha = 0.01$, extinction on (001) = 3° 50', extinction on (010) = 20° 30', angle between a plane s perpendicular to the acute bisectrix and (001) = 79°, angle between the plane s and (010) = 14° 24'.

	SiO ₂ .	Al ₂ O ₃ .	Na ₂ O.	K ₂ O.	CaO.	MgO.	Total.	Sp. gr.
I.	68.47	19.64	11.12	trace	—	—	99.23	—
II.	68.04	20.01	11.09	0.80	0.42	0.12	100.48	2.623
III.	68.49	19.59	11.43	0.40	0.49	—	100.40	2.625
IV.	68.63	20.68	10.55	0.34	0.77	—	101.02	—
V.	66.73	19.87	10.29	0.25	1.22	0.50	98.86	2.623
VI.	66.12	20.88	9.37	0.97	1.89	—	99.23	2.624

* 6 per cent. of Th. (6 per cent. of Tr. in the original).

V. Albite from Mursinka, this corresponding to $Ab : An = 15 : 1$; optic axial angle = $75^{\circ} 30'$, extinction on $(001) = 2^{\circ} 54'$, extinction on $(010) = 17^{\circ} 18' - 17^{\circ} 30'$. VI. Albite from Finland; here $Ab : An = 10 : 1$; extinction on $(001) = 2^{\circ} 30'$, on $(010) = 16^{\circ}$, the position of the acute bisectrix also varies somewhat from that of pure albite.

In these albites there is a connection between the optical characters, but not the crystallographic characters, and the chemical composition. The plagioclastic feldspars are considered neither to form an isomorphous group nor to be double salts, but to be mixtures in various proportions of albite and anorthite, in which the optical characters and the specific gravity vary proportionately with the amounts of these constituents.

L. J. S.

Glauconite. By PETR A. ZEMJATSCHENSKY (*Zeits. Kryst. Min.*, 1896, **26**, 516—517; from *Travaux Soc. Naturalistes St. Petersbourg*, **23**, Sect. d. Géol. et d. Minér., 53—60).—By means of heavy solutions, the author has separated glauconite grains having different characters as regards sp. gr., colour (green to yellow-brown), and the size of the grains. Glauconite is completely decomposed by warm, 10 per cent. hydrochloric acid. On heating to 115° , there is a change in colour and lustre. Green grains, of 0.5—1 mm. diam., from Waywora, gave, on analysis, the results under I. Under the microscope, the material is sometimes seen as an aggregate of six-sided plates, and is distinctly dichroic. Sp. gr. 3.0400. At $100-110^{\circ}$ there is a loss of 2.8268 per cent., at 200° of 1.554.

	SiO ₂ .	Fe ₂ O ₃ , Al ₂ O ₃ .	CaO.	MgO.	K ₂ O.	Na ₂ O.	H ₂ O.	Total.
I.	50.102	31.878	0.437	1.263	2.063	1.451	12.816	100.000
II.	45.751	34.461	0.642	trace	6.840	2.070	11.380	101.144

Dirty olive-green grains from Tschernowskoje (Gov. Nijni-Novgorod) gave analysis II; under pressure, the grains fall to yellowish-brown plates. At $100-115^{\circ}$ there is a loss of 2.816 per cent., at $250-260^{\circ}$ of 6.761. Dark green grains from Tagilj, of sp. gr. 2.8333, lost 3.1847 per cent. at 110° , and 3.8216 at $190-200^{\circ}$. In all the above cases the water was partially regained on exposing the material to the air at the ordinary temperature.

L. J. S.

[**Andalusite or Dumorierite in Argentine Granite.**] By PAUL JANNASCH (*Zeits. anorg. Chem.*, 1896, **12**, 219—222). This mineral forms an amethyst powder, which sinters, but does not melt before the blowpipe, and becomes quite white when heated in a platinum crucible. Sp. gr. = 3.255 at 13.5° . Analysis gave

SiO ₂ .	B ₂ O ₃ .	TiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	CaO.	MgO.	K ₂ O.	Na ₂ O.	H ₂ O.
35.01	2.51	1.08	51.49	1.04	0.28	0.54	3.62	0.96	3.02

It also contains traces of lithium and organic matter.

E. C. R.

Epidote and Zoisite. By ERNST WEINSCHENK (*Zeits. Kryst. Min.*, 1896, **26**, 156—177).—The composition of zoisite approaches to

$\text{H}_2\text{Ca}_4\text{Al}_5\text{Si}_6\text{O}_{26}$, and in epidote the molecule $\text{H}_2\text{Ca}_4\text{Fe}_6\text{Si}_6\text{O}_{26}$ is present in greater proportion, but in the author's klinkzoisite there is actually less iron than in many zoisites. The similarity of the crystal angles of the two minerals is brought out by choosing the following parameters.

	a	:	b	:	c .
Zoisite....	2.9158	:	1	:	1.7900
Epidote...	2.8914	:	1	:	1.8057; $\beta = 81^\circ 3'$.

Groth's view, that zoisite is derived by lamellar twinning from epidote, can be made to agree with the cleavage of the two minerals, but not with their optical properties; while Brögger's view of their morphotropic relationship agrees with neither.

The name *klinkzoisite* is proposed for the monosymmetric members of the zoisite-epidote group, which, in their low content of iron, agree with zoisite in composition, and which are optically positive and have a lower index of refraction and double refraction than ordinary epidote. Analysis I is of rose-red klinkzoisite from the Goslerwand in Prägraten, Tyrol, where it occurs with diopside and potash felspar in a metamorphic rock at a serpentine contact; sp. gr. 3.3720; optical constants under A, positive, $\rho < v$, $a : c = 2^\circ$ in front; the crystal angles agree closely with those of ordinary epidote.

Epidote of a raspberry-red colour from Rothenkopf, Zillerthal, gave analysis II, the iron being here low for epidote; sp. gr. 3.3985; optical constants B.

Light green, columnar zoisite from the Gorner Glacier, near Zermatt, gave III (by A. Schwager), also trace of Cr_2O_3 ; sp. gr. 3.3720; optical constants C. Only the smallest crystals are optically uniform in character; others show irregularly bounded portions with optic axial angles of 90° and 50° in planes at right angles. Emerald-green zoisite from Kleinitz, near Prägraten, gave IV by Nagel, also Cr_2O_3 0.41; sp. gr. 3.3410.

	SiO_2 .	Al_2O_3 .	Fe_2O_3 .	FeO .	MnO .	CaO .	MgO .	H_2O .	Total.
I.	39.06	32.57	1.68	0.29	trace	24.53	—	2.01	100.14
II.	38.60	31.71	3.52	0.35	trace	24.22	—	1.95	100.35
III.	39.31	32.48	2.78	—	—	23.07	0.22	2.54	100.40
IV.	39.42	33.23	1.07	—	—	24.25	—	2.11	100.49

	a .	β .	γ .	$\gamma - a$.	$2V_{Na}$
A	1.7176	1.7195	1.7232	0.0056	$81^\circ 40'$
B	1.7238	1.7291	1.7343	0.0105	89 16
C	1.6973	1.7002	1.7061	0.0088	—

The author considers epidote and zoisite to be dimorphous; klinkzoisite in the epidote series having the same composition as zoisite. The variation of the optical constants with the amount of iron in epidote is pointed out (compare this vol., ii, 371). L. J. S.

Glaucophane from Beaume. By LUIGI COLOMBA (*Zeits. Kryst. Min.*, 1896, **26**, 215; from *Atti Accad. Torino*, 1893-4, **29**, 404-423).
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—Crystals of glaucophane from the schist and limestone at Beaume, an upper valley of the Dora Riparia, Piedmont, gave, on analysis

SiO ₂ .	Al ₂ O ₃ .	FeO.	CaO.	MgO.	Na ₂ O.	K ₂ O.	Total.
56·48	14·60	9·36	2·12	8·27	8·29	trace	99·11

Ferric oxide is present. The primary glaucophane is often altered to chlorite, felspar, and hæmatite. L. J. S.

The Occurrence of Ammoniacal Nitrogen in Ancient Igneous Rocks. By HUGO ERDMANN (*Ber.*, 1896, **29**, 1710—1715).

—The author has found that a number of minerals which occur in ancient igneous rocks evolve ammonia when they are warmed with pure aqueous soda, and has estimated the amount of nitrogen present by converting the ammonia thus evolved into ammonium platino-chloride and weighing the latter. Thus a mineral resembling poly-crase, which occurs in pegmatite near the lake of Ladoga, and which contains oxide of uranium, niobic acid, titanitic acid, and certain of the rare earths, contains 0·028 per cent. of nitrogen evolved as ammonia, whilst another mineral from the same locality, which resembles euxenite, contains 0·005 per cent. of nitrogen. A large number of other minerals from the north of Europe, such as ytter spar from Hitteroe, euxenite from Arendal, fergusonite from Arendal, gadolinite and æschynite from Hitteroe also contain similar quantities of nitrogen. Many of these minerals also contain helium, and the author believes that the latter, like the nitrogen which accompanies it, is present in the form of a compound, and not simply occluded, as supposed by Tilden (*Proc. Roy. Soc.*, 1896, **59**, 218).

Ammonia can also be obtained from carnallite, being most probably derived from an extinct sea fauna. It is possible that the nitrogen of the ancient rocks played an important part in the nourishment of plants in the earlier geological periods. A. H.

Physiological Chemistry.

Composition of Human Fat. By CHARLES A. MITCHELL (*Analyst*, 1896, **21**, 171—173).—The author has investigated the composition of human fat taken from the kidneys.

Excepting the refractive index or the Valenta test, most of the recognised tests were employed. The conclusion is, that the acids of human fat consist of 70 per cent. of liquid acids, principally oleic acid, and 30 per cent. of solid acids, probably palmitic, with small amounts of stearic and myristic acids and traces of lower fatty acids.

L. DE K.

Decomposition of Amygdalin in the Animal System. By ERNEST GÉRARD (*J. Pharm.*, 1896, [6], **3**, 233—236).—The author has determined what digestive ferments react with amygdalin, and has also examined the action of the microbes of the stomach on the same

compound. The thoroughly washed pancreas of a rabbit gave no hydrocyanic acid, and no product which reduced Fehling's solution when kept in an incubator for 80 hours at 36—37°, with 40 c.c. of thymolised water holding 0·4 gram of pure amygdalin in solution. A portion of the small intestine taken 75 cm. from the pylorus when treated in the same way gave reactions of hydrocyanic acid, but no reduction with Fehling's solution. Parts of the intestine near to the cæcum gave the same results. The organisms of the stomach bring about a similar decomposition.

J. J. S.

Chemistry of Vegetable Physiology and Agriculture.

A new Oxydase or Soluble Oxidising Ferment of Vegetable Origin. By GABRIEL BERTRAND (*Compt. rend.*, 1896, **122**, 1215—1217).—The darkening of the juices of beetroot, dahlia, or potato tubers, *Russula nigricans*, &c., is due to the oxidation of the tyrosin under the influence of a soluble ferment. The constitution of tyrosin does not, however, satisfy the conditions of oxidisability through the medium of laccase (Abstr., 1895, i, 386, and this vol., i, 534), and experiment shows that it is not oxidised in presence of laccase. It follows that the phenomena observed must be due to some other ferment, to which the author gives the name *tyrosinase*. It is present not only in dahlia, beetroot, &c., but also in several fungi which contain no tyrosin, and can be extracted in the usual way, the best yield being obtained from certain fungi, and especially from some species of *Russula*. In the case of dahlia and beetroot, the ferment precipitated by alcohol shows but little activity. Direct experiment shows that laccase is without effect on various juices which oxidise readily in contact with tyrosinase, and that the extracts of *Russula*, &c., lose their fermenting power when heated at 100°.

The author gives the generic term *oxydase* to laccase, tyrosinase, and other oxidising ferments of vegetable origin.

Tyrosin can readily be obtained from dahlia roots by adding to the juice one-fourth of its volume of alcohol, filtering off the precipitated ferment as rapidly as possible, allowing the liquid to remain in well closed flasks until the residue is deposited, and then concentrating the mother liquor in a vacuum until the tyrosin crystallises.

C. H. B.

Assimilation of Nitrogen by Moulds. By KONSTANTIN A. PURIEWITZCH (*Chem. Centr.*, 1896, **1**, 125; from *Ber. deut. bot. Ges.*, **13**, 339—345).—*Aspergillus niger* and *Penicillium glaucum* did not grow in nutritive solutions (with cane sugar), free from combined nitrogen; ammonium nitrate was therefore added. Experiments, which lasted for two months, were made in 300—350 c.c. flasks containing 25 or 50 c.c. of nutritive solution. The flasks were sterilised, and the air which was passed through was absolutely free from nitrogen (*sic*). The results of the experiments showed assimilation—

lation of nitrogen, and growth of the mycelium, almost in proportion to the amount of sugar supplied. It is, however, concluded that the amount of nitrogen assimilated by moulds is independent of the amount of dry matter they contain. N. H. J. M.

Mineral Nutrition of Plants. By W. BENECKE (*Chem. Centr.*, 1895, **1**, 792—793; from *Bot. Gen. H.*, **12**, 105—117).—In experiments with *Aspergillus*, *Penicillium*, and *Triticum*, it was found that magnesium is essential for the growth of the fungi and cannot, as stated by Naegeli and Loew, be replaced by calcium, strontium, or barium, by beryllium, as stated by Sestini, or by zinc, or cadmium. In opposition to Naegeli, Loew, and Winogradsky, it was found that rubidium or caesium cannot be substituted for potassium. Similar results were obtained with *Triticum*, for which calcium is also essential as well as sulphur, phosphorus, potassium, magnesium, and iron. Elements with low atomic weights (lithium, beryllium) and with high atomic weights (rubidium, caesium, zinc, cadmium, strontium, and barium) are poisonous. Elements with intermediate atomic weights are indifferent or necessary. This is on the assumption of amounts of the elements to a given surface of the organism, equal to the amounts of magnesium and potassium which are favourable; in a very dilute state, strongly poisonous substances, such as zinc sulphate (Raulin) and copper (Tschirch, this vol., ii, 328) may promote growth. (Compare Sestini, *Abstr.*, 1893, ii, 228). N. H. J. M.

Occurrence of Glutamine in Plants. By ERNST SCHULZE (*Ber.*, 1896, **29**, 1882—1884).—Glutamine can readily be separated from asparagine and tyrosine by crystallisation from water, whilst arginine can be removed by precipitation with phosphotungstic acid. It has been found in many plants, and appears to replace asparagine in many species of cruciferae, in the ferns, and a few others. A. H.

Causes of Loss of Nitrogen in Decaying Organic Matter. By R. BURRI, E. HERFELDT and ALBERT STUTZER (*Chem. Centr.*, 1895, **1**, 501—502; from *J. Landw.*, 1894, **42**, 329—384; compare this vol., ii, 445).—In the preservation of stable manure the chief points are the control of the decomposition of urea and the absorption of ammonia. Loss of nitrogen in the free state will not take place as long as nitrification is suppressed, as for instance by compressing the manure and excluding air.

Bacteria which decompose urea ("ammonia bacteria") are generally present in stables and in all kinds of drainage, &c. Experiments made with the bacteria of liquid manure showed that urea was completely converted into volatile nitrogen compounds by them; they also converted about 22 per cent. of the nitrogen of peptone broth into volatile compounds, whilst pure cultures of "ammonia-bacteria" produced no ammonia from peptone broth. Urea was decomposed with great rapidity, uric acid less quickly, whilst hippuric acid was the least readily decomposed. But even the decomposition of hippuric acid is comparatively rapid when the length of time is considered during which manure is kept. The "ammonia bacteria" of liquid manure are

not affected by strong solutions of ammonium carbonate; the amount of sulphuric acid necessary to destroy them is 0·4 per cent.

N. H. J. M.

Analytical Chemistry.

Apparatus for Gas Analysis. III. By OTTO BLEIER (*Ber.*, 1896, **29**, 1761—1762; compare this vol., ii, 70, 271).—A modification of the apparatus previously described. Close to the three-way tap a short capillary is fused, vertically upwards, it may either be closed with a rod, or connected with a stopcock when in use, this obviates the need of a three-way tap for each additional absorption pipette.

Carbonic oxide is absorbed in two vessels containing, respectively, cuprous chloride dissolved in ammonia, and hydrochloric acid.

A gas pipette for use instead of Hempel's double pipette is also described, it consists of a U-tube with a bulb near the extremity of each limb, the shorter of these is a capillary through which the gas is introduced and it carries a stop-cock at the junction of the capillary and bulb. The longer limb through which the bulbs are filled with the absorbent is closed by a rubber stopper between which and the bulb a short side-tube is fixed, attached to a caoutchouc balloon, which readily enables the capillary to be completely filled with liquid. This pipette is said to be cheaper than, and as efficient as Hempel's.

J. B. T.

Standardising Thiosulphate by Iodic acid. By E. RIEGLER (*Zeits. anal. Chem.*, 1896, **35**, 308).—On treating a solution of thiosulphate with one of iodic acid, the following reaction occurs, $6\text{Na}_2\text{S}_2\text{O}_3 + 6\text{HIO}_3 = 3\text{Na}_2\text{S}_4\text{O}_6 + 5\text{NaIO}_3 + \text{NaI} + 3\text{H}_2\text{O}$, and the smallest excess of iodic acid liberates iodine. Since iodic acid can be obtained absolutely pure, can be completely dried over sulphuric acid, is not hygroscopic, and remains unchanged for a long time when dissolved in water, a N/10 solution, made by dissolving 17.6 grams to a litre, is a very serviceable reagent for standardising thiosulphate.

M. J. S.

Volumetric Estimation of Soluble Iodides. By E. RIEGLER (*Zeits. anal. Chem.*, 1896, **35**, 305—307).—The following reaction occurs between iodic acid and an iodide; $6\text{HIO}_3 + 5\text{NaI} = 5\text{NaIO}_3 + 3\text{H}_2\text{O} + 6\text{I}$. By adding an excess of iodic acid, and titrating the excess by thiosulphate (see preceding abstract) after removal of the free iodine by light petroleum, the amount of iodide is ascertained. The solution of the iodide should not be stronger than 1 per cent. It is mixed with the iodic acid in a stoppered separator bulb, and shaken with two successive portions of light petroleum, after which starch is added and the excess of iodic acid titrated.

M. J. S.

Separation of Ozone from Hydrogen Peroxide, and Recognition of Ozone in the Atmosphere. By CARL ENGLER and W. WILD (*Ber.*, 1896, 29, 1940—1942).—It is found that hydrogen peroxide is immediately decomposed when its vapour is brought in contact with chromic acid, either in the solid state, or in concentrated solution; neither form of the oxidising agent, however, has any action on ozone, and it is possible by this means to completely deprive a mixture containing both substances, of the less stable constituent. The authors propose, therefore, to conduct air through glass beads and chromic acid, and test the gas with the ordinary ozone indicators. M. O. F.

Photometric Method for the Estimation of Lime and of Sulphuric acid. By J. I. D. HINDS (*Chem. News*, 1896, 73, 285—287, 299—300).—By precipitating dilute solutions of sulphuric acid and calcium chloride with solid barium chloride and ammonium oxalate respectively, mixing by pouring from glass to glass, and then observing the length of column required to render the flame of an ordinary candle just invisible; it has been found that with solutions containing from 0.0246 to 0.0055 per cent. of sulphuric acid, and those derived from 0.0333 to 0.0067 per cent. of calcium carbonate, a regular relationship exists between the depth of the column and the quantity of precipitate in suspension, and, consequently, that the former can be taken as a measure of the latter. A constant source of light would be required, and the personal error ascertained before applying the method to practical purposes. The author has made use of the method in the analysis of waters and of urine. D. A. L.

New Method of converting Sulphates into Chlorides. By PAUL JANNASCH (*Zeits. anorg. Chem.*, 1896, 12, 223—224).—The sulphates are fused with four to five times the quantity of boric anhydride, and heated in a platinum crucible until all the sulphuric acid is distilled off. The boric anhydride is then eliminated by means of alcoholic hydrogen chloride (this vol., ii, 576), or it may be treated directly with hydrogen chloride and methylic alcohol; 0.5 gram of sulphate, after 15—30 minutes' fusion, gave no reaction with barium chloride when dissolved in hydrochloric acid. E. C. R.

Action of Fused Polysulphides on Nitrogenous Organic Substances. By HEINRICH AUFSCHLÄGER (*Zeits. anal. Chem.*, 1896, 35, 314—318).—Nitrogenous organic substances, fused with about 2 parts of potassium polysulphide (*hepar sulphuris*, prepared by fusing together 2 parts of potassium carbonate and 1 part of roll sulphur was used) yield considerable amounts of thiocyanate. Upwards of 50 substances belonging to the most widely varied classes were found to give this reaction, which is suggested as a general one for nitrogenous substances; it is obtained even with potassium nitrate, when this is fused with a mixture of potassium sulphide and ignited potassium tartrate. To test for the thiocyanate formed, the cooled melt is dissolved in water and freed from sulphides by zinc sulphate, with addition of some sodium hydroxide. Copper sulphate is then added to the filtrate. Since sulphites are present, no other reducing

agent is required. The cuprous thiocyanate is filtered off, washed, and treated on the filter with ferric chloride. Some quantitative experiments with urea showed that about 10 per cent. of the theoretical yield was obtained.

M. J. S.

Citrate-Soluble Phosphoric acid. By OTTO REITMAIR (*Zeit. angew. Chem.*, 1896, 189—194).—An exhaustive examination of the citrate-solubility question. Wagner's process being purely empirical, great care must be taken to prepare his ammonium citrate solution exactly according to his directions.

Gerlack's solution containing citric acid only, gives in many cases the same results as Wagner's; its use is also more convenient, as it always gives a clear-filtering solution.

L. DE K.

Comparative Methods for estimating Citrate-Soluble Phosphoric acid in Basic Slags. By MAX PASSON (*Zeit. angew. Chem.*, 1896, 286—288).—Basic slags are now tested in Germany by simply estimating their citrate-soluble phosphoric acid; but complaint is being made of serious analytical differences.

The author has found that, when carefully following the conventional (Wagner's) directions, the amount of phosphoric acid dissolved by the ammonium-citrate solution is very constant. The analytical errors are, therefore, most likely caused during the further stages of the process. Excellent results are, however, obtained by the molybdate process if the temperature, during the precipitation, does not exceed 80—85°; if higher, there is a danger of silicic acid precipitating.

The accuracy of Wagner's process is shown by the result of 50 analyses of basic slag, each done in triplicate, using slightly different methods.

L. DE K.

Source of Error as to the presence of, and Estimation of, Boric acid. By GORGES (*J. Pharm.*, 1896, [6], 3, 346—347).—The author draws attention to the fact that the small quantity of boric acid, which is found in so many vegetable products on analysis, is probably introduced by some of the reagents used in the analysis, notably caustic soda and potash. Venable and Callison (*Chem. Zeit.*, 1890, 14, 167) found 0.06 per cent. of boric acid in caustic potash and soda sold as pure; and the author has confirmed their results.

J. J. S.

Decomposition of Silicates by pure Hydrofluoric acid. By ALFRED H. ALLEN (*Analyst*, 1896, 21, 87).—The author decomposes silicates in the following manner:—A mixture of commercial hydrofluoric acid with an equal bulk of sulphuric acid is placed in a large platinum crucible, and into this is placed a smaller crucible containing the silicate, moistened with a few drops of sulphuric acid. After covering the big crucible with a platinum dish filled with cold water, the arrangement is heated on an iron plate, when the acid volatilises, but again drops into the smaller crucible, and then decomposes the silicate. No fixed impurities are introduced into the latter, as is often the case when using commercial acid.

L. DE K.

Decomposition of Silicates by Boric acid. By PAUL JANNASCH and O. HEIDENRICH (*Zeits. anorg. Chem.*, 1896, **12**, 208—218; compare this vol., ii, 219).—One gram of the finely powdered silicate is mixed in a platinum crucible with 3—6 times the quantity of dry powdered boric acid; in the case of fluorspar with eight times the quantity. The mixture is heated gently for 5—10 minutes, to drive off small quantities of water, then fused, and when it is in a state of quiet fusion, it is finally heated over the blowpipe. The fusion is usually finished in about 20—30 minutes. The red hot crucible is then placed on a porcelain triangle, and surrounded with cold water, in order to facilitate the removal of the fused contents. When cold, the fused mass is treated with water (100—150 c.c.) and concentrated hydrochloric acid (50 c.c.), and heated to boiling, when only a few flocks of silica should remain insoluble. The solution is then evaporated to dryness on the water bath; and when it commences to gelatinise is kept constantly stirred.

In order to separate the boric anhydride, the dried mass is treated with methyl alcoholic hydrogen chloride; the latter, which must be freshly prepared, is obtained by treating anhydrous methylic alcohol with dry hydrogen chloride, and then distilling off that portion of the product which comes over at 66—80°. The mixture is now warmed at 70—80° on the water bath, and, after two or three treatments with this liquid, is quite free from boric anhydride. The dry residual salt is heated at 110° for one hour, then lixiviated with hydrochloric acid and water, and the insoluble silica filtered off. The filtrate, which contains 0.5—2 per cent. of the silica, is again evaporated, and treated as above. The analysis of the residue is carried out by the usual methods.

The authors give the results of the analysis of several examples of silicates.

E. C. R.

Behaviour of Minerals of the Andalusite Group towards Decomposing Agents. By PAUL JANNASCH (*Zeits. anorg. Chem.*, 1896, **12**, 219—222).—The decomposition of silicates by means of boric anhydride (see preceding abstract) is of general application, and simpler and more expeditious than the ordinary methods. Disthene, a mineral of the andalusite group, is, however, only partially decomposed by boric anhydride. Minerals of the andalusite group generally behave in an abnormal manner towards decomposing agents, as the author has already pointed out in the case of a mineral allied to andalusite or dumortierite in Argentine granite. When heated with a mixture of calcium fluoride and hydrogen potassium sulphate on a platinum wire, it gives the green boron flame. The finely powdered mineral is only partially decomposed by a mixture of hydrofluoric and sulphuric acids. It can, however, be completely decomposed by ammonium fluoride. The ignited mineral is treated with ammonia, acidified with concentrated hydrofluoric acid evaporated to dryness, and fused for some time in a nickel crucible. The excess of ammonium fluoride is driven off at a higher temperature, and the remaining silicofluoride treated with dilute sulphuric acid.

E. C. R.

Estimation of Potassium. By J. H. VOGEL and H. HAEFCKE (*Landw. Versuchs-Stat.*, 1896, **47**, 97—255).—The shortened method for estimating potassium (*Fresenius Bd.*, **2**, 292) depends on the solubility of the platinochlorides of sodium, calcium, and magnesium, and the insolubility of potassium platinochloride in alcohol. The following average results were obtained by the author, and show the solubility of the potassium salt (at 17—19°) in alcohol of different strengths. Absolute alcohol, 1 : 35196 ; 95 per cent. alcohol, 1 : 31523 ; 80 per cent. alcohol, 1 : 20760. The results, which differ from Precht's (*Zeits. anal., Chem.*, **18**, 509), show that there is no danger of error when about 75 c.c. of absolute alcohol is used for washing, but repeated washing with hot alcohol seems hardly safe. Another weak point in the method is the weighing of the double salt on the filter, or (after redissolving) in a dish ; in drying on a filter there is a danger of partial decomposition of the salt, whilst when the double salt is redissolved in water and evaporated in a dish, large crystals are formed, which require prolonged heating at 130° before the weight becomes constant. These two objections are, however, overcome when the precipitate is collected and weighed in a perforated crucible, as at Halle.

With potassium solutions from which sulphates have been precipitated by barium chloride, errors are readily introduced, owing to the excess of barium chloride forming a platinochloride during evaporation. This is only partly washed out by alcohol, being mostly decomposed thereby ; and the barium chloride formed, which is insoluble in alcohol, remains on the filter with the potassium double salt.

In the method now described (for potassium salts), the substance (10 grams) is dissolved in boiling water (300 c.c.), the volume of the solution being made up to 500 c.c. When cold, 50 c.c. of this solution (= 1 gram of salt) is evaporated nearly to dryness in a platinum dish, and, when cold, treated with 20 c.c. of neutral ammonium carbonate (Schaffgot's) solution, to precipitate the lime and magnesia. After about 12 hours the whole is filtered through a small filter, and washed with 10—15 c.c. of the ammonium carbonate solution. The filtrate is evaporated to dryness in a platinum dish, after adding a very little strong sulphuric acid, and finally heated to redness. The residue is dissolved in hot water, filtered into a porcelain dish, and treated with hydrogen platinum chloride and a drop of dilute hydrogen chloride. It is then evaporated until there is no longer an odour of hydrochloric acid. The cold residue is well rubbed with a mixture of absolute alcohol (2 parts) and ether (1 part), filtered, after 15 minutes, through a well-glazed porcelain Gooch crucible, and washed with some of the mixture. After being dried, the platinum salt is reduced in hydrogen. An apparatus for this purpose is described with sketch. It consists of a Kipp's hydrogen apparatus, to which a Finkener's washing apparatus is attached. The hydrogen passes directly into the crucibles through well fitting covers. The reduction takes place at 240—250°, and too high a temperature must be avoided. After 10—15 minutes, heating is discontinued, but hydrogen is passed through the crucibles until they are cold.

The contents of the crucibles are then extracted with hot water, after which the crucibles are ignited and weighed.

In estimating potash in organic substances, it is not advisable to burn off the organic matter, as there may be a loss of potash by volatilisation. Good results were obtained by decomposing with sulphuric acid, as in Kjeldahl nitrogen determinations. The solution is suitably diluted to a definite bulk, one portion being reserved for estimating nitrogen, another for potash. In estimating potash, the solution is treated first with ammonium carbonate solution, the process being continued, as already described. The ammonium sulphate must, however, be volatilised with great care, using a very small flame; three or four hours will be required for this.

Very exact results are obtained, even when the final amount of platinum is relatively small.

It is of the greatest importance to employ very pure hydrogen platinum chloride, and full directions are given for preparing it. The preparation of the ammonium carbonate solution and of the asbestos for the Gooch crucible are also described. With regard to employing Kjeldahl solutions, it is shown that no potash is dissolved from the glass by prolonged contact with sulphuric acid. N. H. J. M.

Microchemical Reactions [of Barium, &c., and Silver]. By HERMANN TRAUBE (*Zeits. Kryst. Min.*, 1896, **26**, 188—189).—Streng (Abstr., 1886, 487) has proposed to use tartar emetic as a reagent in testing for barium, but it is here pointed out that barium antimony tartrate is not to be distinguished from the strontium and lead salts; also at different temperatures differently hydrated and crystallised salts are obtained. Silver antimony tartrate is characteristic; and silver and lead are the only heavy metals which form crystallised salts. L. J. S.

Estimation of Zinc in Organic Salts. By GOTTFRIED VON RITTER (*Zeits. anal. Chem.*, 1896, **35**, 311—314).—The substance is moistened with concentrated nitric acid, the excess of acid evaporated at a low temperature, and the temperature gradually raised until the residue is burnt white, for which purpose the Lieben muffle is very suitable. Porcelain crucibles must be used, since platinum ones are attacked. M. J. S.

Double Compounds of Aniline and Metallic Salts. By J. L. C. SCHRÖDER VANDER KOLK (*Zeits. anal. Chem.*, 1896, **35**, 297—305).—The crystalline precipitates obtained when many aqueous solutions of metallic salts are shaken with aniline or its aqueous solution can be employed for the micro-chemical detection of such metals. The author has determined the micro-crystallographic properties of aniline sulphate, nitrate and hydrochloride, of ferric and ferrous chlorides, of cobalt and nickel sulphates, nitrates and chlorides, and of the crystalline deposits obtained on treating solutions of these metallic salts with aniline, in the ordinary course of micro-chemical analysis. W. J. P.

Estimation of Tin. By CECIL J. BROOKS (*Chem. News*, 1896, **73**, 218—219).—Finding that stannous salts are more readily oxidised by bromine than by nitric acid, which only acts in strong solutions, and noting the volatility of stannic sulphide, the author recommends the following method for the estimation of tin. The solution is oxidised with bromine, and simultaneously treated with hot hydrogen sulphide solution, and also with the gas; the precipitate is filtered, washed, dissolved in hot ammonium sulphide, concentrated, oxidised with nitric acid, dried, ignited, and weighed. D. A. L.

Occurrence of Iodine in Waters. By MARCO T. LECCO (*Zeits. anal. Chem.*, 1896, **35**, 318—322).—The reaction with nitrous acid and carbon bisulphide is so sensitive that in waters containing no more than 0.1 milligram of iodine in a litre, it can be detected and colorimetrically estimated with sufficient exactness without previous concentration. In waters containing less than this amount, evaporation of a suitable volume to 100 c.c. and filtration before adding nitrite and sulphuric acid is the only preparation required.

By this means, iodine was detected in the mineral waters of Kurschumlija, Lomnitz, and Vrnjze, four springs of the baths of Koviljatscha, and three of the wells of the new Belgrade water supply. Of 12 other Belgrade well waters, which, as a rule, are rich in chlorine, iodine could be detected in only one. The proportion of iodine shows some degree of parallelism with the amount of iron in the waters. M. J. S.

Estimation of Dissolved Oxygen. By GYSBERT ROMIJN (*Rec. Trav. Chim.*, 1896, **15**, 76—80; compare *Abstr.*, 1894, ii, 28).—The author describes a slightly modified form of the method previously given. Instead of using sodium hyposulphite as the reducing agent he employs a solution of manganese chloride (1 mol.) in water, to which Rochelle salt (2 mols.) and an excess of soda solution have been previously added. In the presence of dissolved oxygen the solution soon begins to turn brown, owing to the conversion of the manganous into a manganic salt, and if sufficient of the former be present, the whole of the dissolved oxygen will be used up in 10 minutes. The actual operation is carried out in a pipette, provided at either end with a single way glass stopcock, the upper cock carries a graduated cup, which contains exactly 1 c.c. to the mark. The pipette is filled with the water to be examined by Boot's method (*Abstr.*, 1894, ii, 484). The water is removed from the graduated tube, and this is then filled to the mark with a solution containing 120 milligrams of manganese chloride and 85 milligrams of potassium iodide per c.c. This solution is introduced into the pipette, the tube is rinsed out, the pipette shaken, and then 1 c.c. of a solution of 10 grams Rochelle salt in 12 c.c. water is introduced in exactly the same way, and, finally, 1 c.c. of a solution of caustic soda containing 0.1 gram per c.c. After shaking, the mixture is allowed to remain for six minutes, 1 c.c. of a 25 per cent. hydrochloric acid is added, and the coloured liquid is introduced into a flask, and the free iodine titrated. J. J. S.

Analysis of Anthracene. By HENRY BASSETT (*Chem. News*, 1896, **73**, 178—179).—The sample is oxidised in the usual way, using 15 grams of chromic acid; the next day, it is diluted with 400 c.c. of water, and after three hours is filtered, washed with cold water, and dried in a water oven. The quinone is transferred to a flask with 45 c.c. glacial acetic acid, 2.5 c.c. of chromic acid solution containing 1.5 gram of the acid, and 10 c.c. of nitric acid, sp. gr. 1.420, and boiled for an hour in a reflux apparatus. The following day, it is diluted with 400 c.c. of water, and after three hours is filtered and washed successively with water, boiling 1 per cent. alkali, and hot water. The quinone is dried at 100°, heated for 10 minutes on a water bath with 10 times its weight of pure, concentrated, hot, not fuming, sulphuric acid, left during the night to absorb water in a covered tray of water, diluted, filtered, washed again with water, boiling alkali, and hot water, then dried, weighed, &c. (compare Abstr., 1895, ii, 332).

D. A. L.

Estimation of Phenol in Soaps and Disinfectants. By HEINRICH FRESSENIUS and C. J. S. MAKIN (*Zeits. anal. Chem.*, 1896, **35**, 325—334).—The phenol in dilute aqueous solutions can be distilled with quantitative completeness and estimated in the distillate by Tóth's modification of Koppeschaar's method (Abstr., 1877, i, 746; 1886, 744), which consists in the conversion of the phenol into tribromophenol by treatment with an excess of nascent bromine and titration of the unabsorbed bromine. The soap is dissolved in water, decomposed by a small excess of sulphuric acid, and the whole distilled with the help of a rapid current of steam, which considerably shortens the operation. Although traces of fatty acids pass over and consume bromine, their amount is so small that it may be neglected in practice. It, however, increases as the time of distillation is prolonged.

For disinfecting powders, which consist essentially of lime and carbolic acid, 0.5 gram is mixed with water in the distillation flask, and strongly acidified with hydrochloric acid before distilling.

The distillate is mixed in a stoppered flask with an excess of solution of sodium bromide and bromate. Hydrochloric acid is added, and the mixture shaken for 30 minutes. An excess of potassium iodide is then added, and, after 12 hours, the liberated iodine is titrated. Six atoms of bromine are consumed by one molecule of phenol.

M. J. S.

Estimation of Pentoses and Pentosanes by the Furfuraldehyde Distillation Process. By BERNHARD TOLLENS (*Zeit. angew. Chem.*, 1896, 194—195).—The author (this vol., ii, 393) recommended distilling the substance with hydrochloric acid, and precipitating the furfuraldehyde with phloroglucinol.

For calculating furfuraldehyde to pentosanes in general, the factor 1.84 is now proposed.

L. DE K.

Estimation of Sugars by Fehling's Solution. By JOHAN G. C. T. KJELDAHL (*Zeits. anal. Chem.*, 1896, **35**, 344—368; from *Meddelelser*

fra Carlsberg Laboratoriet, 4, 1).—The amount of cuprous oxide precipitated by identical quantities of sugar is largely influenced by the area of the surface of the liquid exposed to the air during the heating, as well as by the length of the boiling and the amount of copper solution employed. The following mode of procedure was, therefore, uniformly adopted. The requisite amount of Fehling's solution (usually 30 or 50 c.c., 15 c.c. being used only for very weak sugar solutions) was placed in a conical flask of 150 c.c. capacity. The measured quantity of sugar solution was added, and then water to exactly 100 c.c. The air was then excluded by passing hydrogen through the liquid until the end of the heating, and the flask was heated for exactly 20 minutes on the boiling water bath. The cuprous oxide was filtered off and weighed as usual, contact of air during this stage having far less influence than during the heating. The Fehling's solution was of the ordinary strength, but it is recommended that the three constituents should be kept apart until the time of use, when the solid tartrate should be dissolved in the soda solution. The exact proportions of tartrate and sodium hydroxide (65 grams per litre) must be adhered to.

The relation between the amount of copper reduced (Cu) and the sugar present (S) may now be expressed by the equation $Cu = aS - bS^2$, and the values of the factors a and b in the following table have been calculated from the experimental numbers by the method of least squares.

Volume of Fehling's solution, c.c.	Dextrose.		Levulose.		Galactose.		Arabinose.		Lactose, $C_{12}H_{22}O_{11} + H_2O$.		Maltose, $C_{12}H_{22}O_{11}$.	
	a .	$b \times 10^4$.	a .	$b \times 10^4$.	a .	$b \times 10^4$.	a .	$b \times 10^4$.	a .	$b \times 10^4$.	a .	$b \times 10^4$.
15	2.2816	70.162	1.9545	31.058	2.0089	46.851	2.2924	63.480	1.5031	16.922	1.3496	14.7850
30	2.3096	33.174	2.0654	22.750	2.0614	22.938	2.2506	25.192	1.5249	10.991	1.3143	6.9110
50	2.3300	20.490	2.1065	14.690	2.0937	14.626	2.2772	16.946	1.4296	4.1835	1.2322	3.0504
75	2.2786	12.333	2.0825	9.0112	2.0613	9.009	2.2695	11.615	1.3656	2.0120	—	—
100	2.2240	8.198	2.0658	6.3146	2.0087	5.871	2.1910	7.235	1.3340	1.3361	1.1305	1.0305

Extended tables for economising calculation are also furnished. When two sugars (for example, glucose and maltose) are present, the amount of copper they reduce jointly is expressed by the equation $p = \frac{px}{g} + \frac{py}{m}$, where p is the total amount of copper reduced, g the corresponding amount of glucose taken from the table, m the corresponding amount of maltose, x and y the respective amounts of glucose and maltose present. By making two determinations with different volumes of Fehling's solution, and using in the second case a multiple (n) of the amount of sugar used in the first, a second equation, $P = \frac{P}{G}nx + \frac{P}{M}ny$, can be obtained; whence

$$x = \frac{nm - M}{n\left(\frac{m}{g} - \frac{M}{G}\right)} \text{ and } y = \frac{ng - G}{n\left(\frac{g}{m} - \frac{G}{M}\right)}$$

In opposition to E. Fischer (Abstr., 1895, i, 6), the author has confirmed by fresh experiments his original statement that maltose is not changed by yeast mixed with thymol. He cannot, however, confirm Jais' assertion that maltose is not attacked when heated with 70—100 parts of N/40 hydrochloric acid. M. J. S.

Estimation of Glucose. By HENRI E. CAUSSE (*J. Pharm.*, 1896, 3, 433).—In consequence of the publication of Gerrard's method for the estimation of glucose (this vol., ii, 225), the author calls attention to the fact that he has already recommended a similar method (Abstr., 1889, 1036), employing potassium ferrocyanide instead of potassium cyanide. The author considers his own method the more delicate and trustworthy. J. J. S.

Examination of Honey. By ERNST BECKMANN (*Zeits. anal. Chem.*, 1896, 35, 263—284).—The products of the action of acids on starch are the substances most generally employed in the adulteration of honey. Since in the manufacture of starch syrup the hydrolysis is carried on only to the point where iodine gives a red reaction, erythrodextrin and amylopectin are commonly present, and may be precipitated from the adulterated honey by the addition of methylic alcohol to its concentrated aqueous solution. Both dextrorotatory (flower) and levorotatory (conifer) honeys are almost entirely soluble in methylic alcohol. Honey containing starch syrup is coloured red to violet by iodine solution, whereas pure honey gives no such colour. If the hydrolysis of the starch has been carried so far that iodine no longer gives any coloration, as in the manufacture of solid starch sugar, no precipitate is produced by methylic alcohol. Such starch sugar, however, still contains dextrinoid substances, which yield barium compounds insoluble in methylic alcohol, whilst the dextrans of natural honey give no precipitate, or, in the most unfavourable case, that of conifer honey, only about 2.5 per cent. For qualitative testing, 5 c.c. of a solution containing 20 grams of honey in 100 c.c. is shaken in a test tube with 2 c.c. of a 2 per cent. baryta solution and 17 c.c. of methylic alcohol, a comparative experiment with a pure honey, of about the same dextrin content, being advisable in doubtful cases. For quantitative estimation, the baryta precipitate should be collected on a Gooch filter, washed first with 10 c.c. of methylic alcohol, then with 10 c.c. of ether, and dried at 55—60°. The more rapidly the whole operation is performed the better. The results obtained with specially prepared mixtures of conifer honey with starch syrup and sugar show that the fact of adulteration can in all cases be detected, although they do not suffice for the calculation of its amount. In doubtful cases, a combination of the fermentation process, using a feebly acting yeast (beer yeast, or yeast of the Saatz type), by which the dextrans of natural honey are more completely fermented than those of starch products, may be resorted to.

The addition of molasses to honey is best detected by examining for raffinose with basic lead acetate (1 part of lead acetate, 3 parts of litharge, and 10 parts of water) and methylic alcohol. The honey solution should not be stronger than 25 per cent., and for 5 c.c. of the solution 2.5 grams of basic lead acetate and 22.5 c.c. of methylic alcohol are employed. Conifer honey gives 1 per cent., molasses 50—70 per cent., of lead precipitate.

M. J. S.

Detection of Formalin. By HENRY DROOP RICHMOND and L. KIDGELL BOSELEY (*Analyst*, 1896, **21**, 92—94).—The authors recommend Hehner's test as being the most delicate test for formylaldehyde in milk; far more sensitive even than their own test with diphenylamine (Abstr., 1895, ii, 426).

The test is best applied by first diluting the sample with an equal bulk of water, and then carefully adding sulphuric acid of 90—95 per cent. strength. If formylaldehyde is present, a violet ring is formed where the two liquids meet.

L. DE K.

Detection of Formalin. By OTTO HEHNER (*Analyst*, 1896, **21**, 94—97).—The author finds that the blue colour developed when milk containing formylaldehyde is mixed with sulphuric acid is due to the presence of the casein.

To test wine or vinegar for this preservative, a drop of milk is added to the sample, and the mixture is poured carefully on to sulphuric acid contained in a test tube. A blue ring will then form if formylaldehyde is present.

L. DE K.

Estimation of Formaldehyde. By HARRY M. SMITH (*Analyst*, 1896, **21**, 148—150).—The sample is mixed with aqueous potash until the amount of alkali is about 10 per cent. Solution of potassium permanganate, 5.26 grams per litre, is now slowly run in until the green colour disappears rather slowly, and the liquid is then heated to 30° to cause the precipitate to subside. More permanganate is then added until an olive-green colour is obtained permanent for 15—20 seconds. At this stage, when the aldehyde has been converted into formic acid, 1 c.c. of the permanganate = 0.0015 gram of formaldehyde.

As a check, the mixture may now be boiled, and the adding of permanganate be continued until an emerald-green colour is obtained, lasting at least 10 minutes. At this stage, the formic acid now being completely converted into carbonic acid, 1 c.c. of the permanganate = 0.0075 of formaldehyde.

L. DE K.

Estimation of Tartar and Tartaric acid in Wine. By B. HAAS (*Zeits. anal. Chem.*, 1896, **35**, 376; from *Zeits. Nahrungsmittel-Unters. und Hygiene*, **2**, 97).—In each of two porcelain basins is placed 50 c.c. of the wine, the acidity of which has previously been ascertained, and to one of these portions is added enough potassium carbonate solution to neutralise exactly half the free acid present. Both liquids are now evaporated to 3—5 c.c., adding to the half neutralised one 2 c.c. of glacial acetic acid for each gram of tartaric

acid neutralised. 100 c.c. of 95 per cent. alcohol is gradually, and with stirring, added to each residue. After two hours, the precipitates are collected on a filter, washed with 95 per cent. alcohol, and then titrated with potash in hot aqueous solution, using litmus tincture as indicator. The unneutralised portion gives the tartar, and the difference between the two the tartaric acid. M. J. S.

Composition and Analysis of Commercial Cream of Tartar.

By ALFRED H. ALLEN (*Analyst*, 1896, 21, 174—180, 209).—The author, after criticising the B.P. tests for cream of tartar, finally proposes the following process. 1·881 gram (or in important cases double this quantity) of the *dried* sample is dissolved in hot water and titrated with N/10 alkali and phenolphthaleïn. In absence of other acid substances, 1 c.c. of the alkali represents 1 per cent. of potassium hydrogen tartrate. The same amount is ignited, but without attempting to burn off the carbon. The mass is boiled with water, and the filtrate is titrated with N/10 hydrochloric acid and methyl-orange. When dealing with a pure sample, the number of c.c. of acid will correspond exactly with the c.c. of alkali used in the first experiment, but each c.c. of deficiency represents 0·36 per cent. of calcium sulphate, or 0·72 per cent. of potassium hydrogen sulphate. Any excess points to the presence of potassium tartrate, each c.c. representing 0·60 of this compound. The sulphate may be, of course, estimated by means of barium chloride.

The insoluble matter is ignited to burn off the carbon, and the ash is dissolved in 20 c.c. of N/10 acid, any insoluble residue, such as sand, or barium sulphate being filtered off, and the liquid titrated with N/10 alkali and methyl-orange. Each c.c. corresponds with 0·5 per cent. of calcium tartrate or 0·3 per cent. of calcium sulphate.

L. DE K.

Titration of Quinine. By ALFRED H. ALLEN (*Analyst*, 1896, 21, 85—87).—The author points out that commercial quinine sulphate is neutral towards brazil wood, logwood, and cochineal, distinctly alkaline to litmus, and strongly so to methyl-orange.

When titrating with the last indicator, double the amount of standard acid will be required.

L. DE K.

A New Reaction for Antipyrine or for Quinine. By C. CARREZ (*J. Pharm.*, 1896, [6], 3, 253—255).—When a mixture of equal parts of antipyrine and quinine is treated with bromine water and then with ammonia, a red coloration is obtained which is given by neither of the alkaloids separately. This red compound, *quinerythropyrine*, is best extracted from its ammoniacal solution by means of chloroform. It is only slightly soluble in pure water, but readily in acidified water. With acids, it gives an orange-rose colour, and with alkalis a violet-rose. The reaction can be made use of in testing for quinine or for antipyrine, and is also applicable for urine testing.

J. J. S.

General and Physical Chemistry.

Spectrum of Phosphorus in Fused Salts and certain Metallurgical Products. By ARNAUD DE GRAMONT (*Compt. rend.*, 1896, **122**, 1534—1536).—When fused phosphates are subjected to the action of a condensed spark (next abstract), a line spectrum of phosphorus is obtained superior to that seen in a Plücker's tube. With sodium or potassium phosphate, the following lines are observed, and are bright and distinct except where otherwise indicated: 6506 (diffuse), 6458, 6088, 6042, 6034·5, 6025, 5498·5, 5462 (feeble), 5453 (feeble), 5423·5, 5409, 5385, 5340, 5311, 5292, 5250, 4968 (diffuse), 4941, 4603, 4588·5. The lines most easily recognised are the triplet, 6042-6034·5-6025, in the red, and the doublet, 4603-4588·5, in the blue. This spectrum is seen in many metallurgical products containing phosphorus—and especially in copper phosphides when these are examined in the manner previously described (*Abstr.*, 1895, ii, 470). The brightness of the lines diminishes with the proportion of phosphorus, and the characteristic triplet in the red becomes invisible in metals when the percentage falls to between 1·0 and 0·1 of phosphorus. C. H. B.

Dissociation Spectra of Fused Salts of Alkali Metals. By ARNAUD DE GRAMONT (*Compt. rend.*, 1896, **122**, 1411—1413).—Salts of alkali metals offer special advantages in the study of the line spectra of the non-metals by the action of a highly condensed spark on the fused salt, because of the comparative simplicity of the spectrum of the metal. In the case of these salts, the spectrum with a highly condensed spark differs considerably from that obtained with the spark and the metal itself, or with the fused salt and a non-condensed spark. The carbonates, although dissociated with difficulty, give the spectra of the metals in their simplest form, and no lines of carbon are observed. Fluorides also show relatively little tendency to dissociate, but other salts, such as chlorides, bromides, and iodides, decompose readily.

Sodium salts show the three intense doublets—6160-6154, 5895-5889, 5687-5682, whilst all other lines are feeble, though 5675, 5669, 5155, 5152, and a broad diffuse band, 4983-4978, are recognisable.

Potassium salts show 7698, 7665, 6939, 6911, 6308, 6245·5, 6117·5, 5832, 5811, 5801, 5783, 5360, 5344, 5340, 5323, 5113, 5099, 4828, 4389, 4309, 4264, 4223, 4185, 4045, although the first two are difficult to see.

Lithium salts show 6706, 6103, 4972, 4603, 4273, 4132, and the small number of lines shown by this metal makes its salts particularly suitable for investigations of the spectra of the non-metals.

C. H. B.

“Convection” Currents. By FRANZ RICHARZ and CARL LONNES (*Zeit. physikal. Chem.*, 1896, **20**, 145—158).—The authors endeavour.

voured to determine the cause of the currents through acidified water, which occur with electromotive forces insufficient for the decomposition of the water. As hydrogen peroxide is produced with a stronger E.M.F., they considered it probable that a similar formation might also be the cause of the convection currents. Preliminary experiments showed that the peroxide is not produced when the platinum and gold electrodes employed are placed in acidified water, although they contained occluded hydrogen. During the passage of the convection currents, however, hydrogen peroxide is formed, but the quantity produced is insufficient to account for the current, neither is it in any way proportional to the current strength as measured by a silver voltameter. The peroxide is not produced with an E.M.F. below that of one Daniell's cell. Experiments with solutions of sodium hydroxide showed that sodium peroxide is formed at the cathode, but no barium peroxide is produced in solutions of barium hydroxide.

L. M. J.

Electromotive Force and Partition Equilibrium. By ALFRED H. BUCHERER (*Zeit. physikal. Chem.*, 1896, **20**, 328—330).—The author claims to have made several of the observations recorded by Luther (this vol., ii, 461), and to have drawn similar conclusions at an earlier date, his results having appeared in the *Electrochem. Zeit.* for January, and in the *Chemiker Zeitung* of January 4th.

L. M. J.

The Potential Differences at the Surface of Contact of Dilute Solutions. By OLIN FREEMAN TOWER (*Zeit. physikal. Chem.*, 1896, **20**, 198—206).—By calculating the potential difference between $\text{HNO}_3(1) - \text{HNO}_3(2)$ by means of Nernst's formula, and subtracting this from the E.M.F. of the galvanic chain $\text{MnO}_2 - \text{HNO}_3(1) - \text{HNO}_3(2) - \text{MnO}_2$, the sum of the potential differences between the acids and electrodes can be obtained. Also, by means of approximations in Planck's formula, the potential differences, $\text{HNO}_3(1) - \text{KCl}$ and $\text{KCl} - \text{HNO}_3(2)$, can be ascertained, and, by adding these to the previous results, the E.M.F. of the chain $\text{MnO}_2 - \text{HNO}_3(1) - \text{KCl} - \text{HNO}_3(2) - \text{MnO}_2$ can be calculated. This was done with chains in which not only potassium chloride but also sodium chloride and sodium nitrate at concentration 1 to 1/128 normal were employed, and in all cases there was satisfactory agreement between the calculated numbers and the observed E.M.F. In all cases the presence of the salt solution diminished the negative potential difference between the acids, and so increased the E.M.F. of the cell; this effect increasing with the concentration of the salt. In the case of similar experiments with zinc electrodes in solutions of zinc nitrate, the agreement was not so satisfactory, possibly owing to Planck's formula being available only for univalent ions, for which the previous experiments prove its validity.

L. M. J.

Electrolytic Decomposition of Fused Zinc Chloride. By RICHARD LORENZ (*Zeit. anorg. Chem.*, 1896, **12**, 272—276).—A determination of the voltage required to decompose pure fused zinc chloride gives the number 1.49 to 1.50 volts. Three different strengths

of current were employed in the experiments, and the results obtained from each agree closely. The theoretical voltage = 2.1, but it must be remembered that the temperature at which the experiments were carried out was 500—600°. E. C. R.

Influence of Ethylic Alcohol on the Electrolytic Dissociation of Water. By RICHARD LÖWENHERZ (*Zeit. physikal. Chem.*, 1896, **20**, 283—302).—The author has re-determined the electrolytic dissociation of water by Ostwald's method (Abstr., 1893, ii, 365), using, also, a correction for the difference of potential between acid and base as indicated by Nernst (Abstr., 1894, ii, 343).

The apparatus employed was similar to that described by Smale (Abstr., 1894, ii, 436). Owing to the variations, the values for the E.M.F. could not be considered accurate to the extent of more than 1/1000 volt. Solutions of acid and alkali of N/10 and N/100 were employed, and the values for the dissociation thus obtained were 1.075×10^{-7} , 1.187×10^{-7} , and 1.134×10^{-7} , numbers agreeing well with the results of Wijs, Arrhenius and Shields, and Kohlrausch; on the addition of ethylic alcohol, however, the dissociation was found to decrease, the following values being obtained.

7.4 p. c.	— 0.92×10^{-7} .	86.6 p. c.	— 0.0574×10^{-7} .
24.0 „	— 0.69×10^{-7} .	92.6 „	— 0.0270×10^{-7} .
41.8 „	— 0.470×10^{-7} .	97.4 „	— 0.0096×10^{-7} .
64.8 „	— 0.201×10^{-7} .	99.8 „	— 0.00288×10^{-7} .

The results indicate that in solutions of little water in much alcohol, the water obeys the law of feebly dissociated electrolytes, that is, the concentration of the ions is proportional to the square root of the water concentration. In stronger solutions, however, the dissociation is greater than indicated by the law, and the water is shown to have a stronger dissociating influence on its own molecules than the ethylic alcohol has. L. M. J.

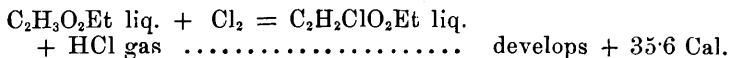
New Method of determining Freezing Points. By MEJER WILDERMANN (*Proc. Roy. Soc.*, 1896, **59**, 251—254).—The author discusses the best means of determining freezing points in dilute as well as in concentrated, solutions. The proper arrangement of equilibrium in the heterogeneous system is first mathematically considered, and the proper treatment of the instrument used for measuring temperature is explained. H. C.

Freezing Point Depressions in very Dilute Solutions. By RICHARD ABEGG (*Zeit. physikal. Chem.*, 1896, **20**, 207—233).—The freezing points of a number of solutions were determined, a full account of the apparatus and method being given in the paper. The preliminary experiments indicated the necessity of maintaining a constant rate of stirring, as variations caused a marked difference in the Newtonian constant k of the equation $dt = k(t_0 - t)/dz$ (where t_0 = convergence temperature, Abstr., 1895, ii, 155). Experiments with potassium chloride and cane sugar further show that the value of k is not constant for different solutions, so that the conclusions of

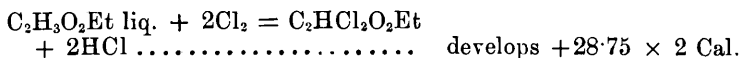
Wildermann (this vol., ii, 291) are not valid. The value of t_0 was in all cases only slightly lower ($<0.5^\circ$) than the actual freezing point of the solution, so that the error due to this difference, which was found to be about 2 per cent. per degree, cannot exceed 1 per cent., and the results are therefore not further corrected. Several series of experiments were performed with very dilute solutions of each compound, and the mean of each series taken. The values for the molecular depression thus obtained are: cane sugar, 1.89, 1.82, 1.89, 1.845; alcohol, 1.78, 1.79; urea, 1.86, 1.875; dextrose, 1.78, 1.84; tartaric acid, 1.83, 1.84. In the case of electrolytes (potassium chloride, sodium chloride, and potassium sulphate) the dissociation was calculated with the value 1.85 for the molecular depression, and the results obtained are compared with those derived from the conductivity. The agreement is satisfactory, but the cryoscopic values are generally the higher.

L. M. J.

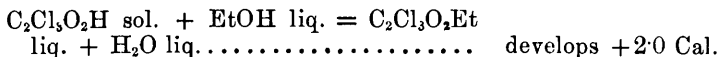
Ethylic Salts of the Chloracetic acids. By PAUL RIVALS (*Compt. rend.*, 1896, 122, 1489—1491).—*Ethylic Chloracetate*.—Heat of combustion (1 gram) +4029.1 Cal.; molecular heat of combustion at constant volume +493.56 Cal., at constant pressure +493.85 Cal.; heat of formation of the liquid from its elements, +129.75 Cal.



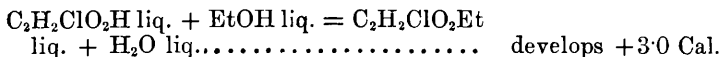
Ethylic Dichloracetate.—Heat of combustion (1 gram) +2951 Cal.; molecular heat of combustion at constant volume and at constant pressure, +463.31 Cal.; heat of formation of the liquid from its elements, +130.7 Cal.



Ethylic Trichloracetate.—The heat of formation of this compound was determined indirectly by the action of trichloroacetic chloride on ethylic alcohol.



From the data already given it follows that



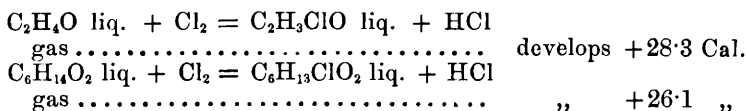
The substitution of chlorine for hydrogen in acetic acid increases the energy of the acid function, and the chloracetic acids in this respect resemble formic acid and the more energetic organic acids (compare Abstr., 1895, ii, 254).

C. H. B.

Acetal and Monochloroacetal. By PAUL RIVALS (*Compt. rend.*, 1896, 122, 1488—1489).—*Acetal*.—Heat of combustion (1 gram), +7802 Cal.; molecular heat of combustion at constant volume, +920.7 Cal. at constant pressure, +923.2 Cal.; heat of formation of the liquid from its elements, +125.6 Cal.

Chloroacetal.—Heat of combustion (1 gram), +5825 Cal.; molecular heat of combustion at constant volume, +888·31 Cal., at constant pressure, +889·70 Cal.; heat of formation of the liquid from its elements +129·7 Cal.

From these and previous results (compare Abstr., 1895, ii, 306) it follows that



and hence the heat of formation of chloroacetal from monochloroaldehyde and alcohol (−4·0 Cal.) is practically equal to the heat of formation of acetal from aldehyde (−2·3 Cal.). In other words the substitution of chlorine for hydrogen in aldehyde has no appreciable influence on the heat of formation of the ethylic derivatives of aldehyde.

C. H. B.

Heat of Vaporisation of Formic acid. By DOROTHY MARSHALL (*Compt. rend.*, 1896, **122**, 1333—1335).—The heat of vaporisation of carefully purified formic acid was determined by the method of comparison (this vol., ii, 349), the other liquid being benzene. The value obtained is 120·36, which agrees with that obtained by Favre and Silbermann, 120·7. The quotient of the molecular heat of vaporisation by the absolute temperature ML/T , is 14·7, which is identical with the corresponding number for acetic acid.

The value of the latent heat of vaporisation of formic acid, calculated by Raoult's formula, from his observations on its vapour tension, is 120·9.

C. H. B.

Heat of Dissolution of Sodium Chloride. By ED. VON STACKELBERG (*Zeit. physikal. Chem.*, 1896, **20**, 159—167).—From the experimental data of Winkelmann and Staub, tables are derived and curves constructed for (1) the heat of dissolution of sodium chloride at various concentrations; (2) the total heat of dissolution up to these concentrations, at temperatures 18° and 0°. The curves (1) cut the concentration 35·5 per cent. ordinate at about +1·2 Cals. and −4 Cals., so that at 0° the heat of dissolution in a concentrated solution is negative, but positive at 18°, results which agree with the observations of Braun and Deventer. The curves, moreover, cut at about 20 per cent., so that it follows that the temperature coefficient of the heat of dissolution is negative in dilute solutions, but becomes positive at higher concentrations, a result which is also shown to obtain with solution of sodium nitrate, potassium nitrate, potassium chloride, and ammonium chloride. Corresponding with the change from the positive to the negative value in curve (1), the curve for the total heat of dissolution at 0° reaches a maximum at about 25 per cent., after which it decreases.

L. M. J.

Thermochemistry of Uranium Compounds. By J. ALOY (*Compt. rend.*, 1896, **122**, 1541—1543).—*Heats of Dissolution at*

18—20°.—Uranium nitrate, $\text{UO}_2(\text{NO}_3)_2 + 3\text{H}_2\text{O}$, -3.7 Cal.; sulphate, $\text{UO}_2\text{SO}_4 + 3\text{H}_2\text{O}$, $+5.1$ Cal.; chloride, $\text{UO}_2\text{Cl}_2 + \text{H}_2\text{O}$, $+6.05$ Cal.; chromate, $\text{UO}_2\text{CrO}_4 + 5\frac{1}{2}\text{H}_2\text{O}$, -6.3 Cal.; acetate, $\text{UO}_2(\text{C}_2\text{H}_3\text{O}_2)_2 + 2\text{H}_2\text{O}$, -4.3 Cal.; uranyl potassium chloride, $\text{UO}_2\text{Cl}_2 \cdot 2\text{KCl} + 2\text{H}_2\text{O}$, $+2.0$ Cal.; uranyl ammonium acetate, $\text{UO}_2(\text{C}_2\text{H}_3\text{O}_2)_2 + \text{NH}_4 \cdot \text{C}_2\text{H}_3\text{O}_2 + 6\text{H}_2\text{O}$, -3.8 Cal.

Uranyl hydroxide, $\text{UO}_2(\text{OH})_2$, was prepared by evaporating a solution of the nitrate in absolute alcohol (Malaguti), and by heating the nitrate on a sand bath (Berzelius). Both products had the same composition, and gave the same thermal disturbances when dissolved in acids. The heats of neutralisation with two equivalents of various acids at 19°, were as follows: Hydrochloric, $+8.4$ Cal.; hydrobromic, $+8.8$ Cal.; nitric, $+8.4$ Cal.; sulphuric, $+9.5$ Cal.; acetic, $+7.5$ Cal.

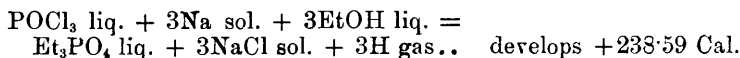
The heats of formation of the uranyl salts from the hydroxide are lower than those of zinc and lead salts, and approximate to those of the ferric and chromic salts.

C. H. B.

Measurement of the Heat of Formation of Triethylic Phosphate by the Action of Phosphorus Oxychloride on Sodium Ethoxide. By J. CAVALIER (*Compt. rend.*, 1896, **122**, 1486—1488).—When phosphorus oxychloride is added to a solution of sodium in excess of dry alcohol, there is an immediate energetic action with formation of sodium chloride and triethylic phosphate. The following measurements were made.

Heat of dissolution of sodium in alcohol ($\text{Na} + 12\text{EtOH}$).....	$+42.88$ Cal.
POCl_3 liq. $+ 3\text{EtONa}$ diss. $= \text{Et}_3\text{PO}_4$	
diss. $+ 3\text{NaCl}$ pptd.....	develops $+109.77$ „
Heat of dissolution of triethylic phosphate in alcohol	-0.20 „

From these results, it follows that



and combining this result with the known data involved,



a result comparable with that obtained in the case of alcohol and acetic acid.

C. H. B.

Diffusion of Metals. By WILLIAM CHANDLER ROBERTS-AUSTEN (*Phil. Trans.*, 1896, **187**, 383—415. “Bakerian Lecture”).—Very little attention has been given hitherto to the consideration of the molecular movements which enable two or more molten metals to mix spontaneously and form a truly homogeneous fluid mass. Some experiments on the mobility of gold and silver in molten lead, made by the author about 14 years ago and communicated to the Chemical Section of the British Association in 1883, appear to be the first ever

made with the direct object of investigating the diffusion of molten metals and alloys, other than those of mercury which are liquid at the ordinary temperature. The research has been resumed during the past two years, and the diffusion of various metals in molten lead, bismuth, and tin has been carefully investigated.

The tubes which contain the molten metal are arranged in an air bath with double walls, which can be readily maintained at definite temperatures, the measurement of the temperature being effected by the aid of thermo-junctions. The tubes are carefully kept hotter at the top than at the bottom, so as to avoid convection currents from the bottom of the tube. At the end of a given period, varying from six hours to seven days, the diffusion tubes were removed, cooled from below, carefully measured, and then cut into transverse numbered sections, the metallic contents of each section being weighed and analysed.

According to Fick, who applied Fourier's theory of thermal conduction to the phenomena of material diffusion generally, the movement in linear diffusion may be expressed by the differential equation—

$$dv/dt = k(d^2v/dx^2).$$

In this equation, x represents the distance in the direction in which the diffusion takes place; v is the degree of concentration of the diffusing metal, and t the time; k is the diffusion constant, that is the number which expresses the quantity of the metal, in grams, diffusing through unit area (1 sq. cm.) in unit time (one day), when unit difference of concentration (in grams per c.c.) is maintained between the two sides of a layer 1 cm. thick. The unit of diffusivity has the dimensions [L^2T^{-1}], so that diffusion constants may be expressed in square centimetres per day. The constant has a definite value for each pair of metals (that is for the diffusing metal and its solvent) at a particular temperature, and the object of the experiments on diffusion is to determine this value. It was found that the tables calculated by Stefan for the diffusion of salts apply in the present instance. By the help of these tables, the diffusion constant could be determined when the distribution of the dissolved diffusing metal was known.

In the following table, the results of the more recent experiments are recorded.

It will be seen that gold diffuses more rapidly in bismuth and in tin than it does in the heavier metal lead. It has also been observed that platinum diffuses faster in bismuth than in lead. The diffusion of platinum and of gold is increased in about equal ratio by the substitution of bismuth for lead as a solvent. On the other hand, platinum diffuses much more slowly in lead than gold does, although their atomic weights and their densities do not greatly differ. Rhodium, another metal of the platinum group, diffuses in lead nearly as fast as gold does; but if allowance be made for the smaller atomic weight, it will be found to agree fairly well with platinum. This would point to the conclusion that the platinum metals are molecularly more complex than either gold or silver, as a complex

molecule exerts less osmotic pressure and diffuses more slowly than a comparatively simple one.

Diffusing metal.	Solvent.	Temperature.	k in square centimetres.	
			Per diem.	Per second.
Gold	Lead.....	492°	3·00	3·47 × 10 ⁻⁵
"	"	492	3·07	3·55 "
Platinum	"	492	1·69	1·96 "
"	"	492	1·69	1·96 "
Gold	"	555	3·19	3·69 "
"	Bismuth ...	555	4·52	5·23 "
"	Tin	555	4·65	5·38 "
Silver	"	555	4·14	4·79 "
Lead	"	555	3·18	3·68 "
Gold	Lead	550	3·185	3·69 "
Rhodium	"	550	3·035	3·51 "

The diffusion of metals is not increased nearly so rapidly by a rise in temperature of 50° as the ordinary aqueous diffusion of salts is. It may be that the molecules of the diffusing substance are not so liable to disruption by a rise in temperature.

A number of experiments were made on the diffusion, at ordinary temperature, of gold in mercury, the value found for k at 11° being 0·72 sq. cm. per day. From experiments by Guthrie (1883) on the diffusion of zinc, tin, lead, sodium, and potassium in mercury, the following values for k , in square centimetres per day, were calculated.

Tin in mercury at about 15°.....	1·22
Lead " "	1·0
Zinc " "	1·0
Sodium " "	0·45
Potassium in mercury at about 15°.....	0·40

The experiments described in the first part of this paper naturally suggested the inquiry whether gold would still permeate lead if the temperature were maintained at a point far below the melting point of lead. The attempt was first made to ascertain whether diffusion of gold in solid lead could be measured at 250°, that is 75° below the melting point of lead. Thin plates of gold were fused on to the end of cylindrical rods of lead, 14 mm. in diameter and 7 cm. long. Such cylinders were maintained at 250° for 31 days in a little iron chamber lined with asbestos. They were then measured and cut up into sections, and the amount of precious metal in the respective sections was determined by analysis. In each case gold was found throughout the entire length of the cylinder, and the diffusivity was found in one case to be 0·023 and in another 0·03 sq. cm. per diem.

Similar results were obtained in experiments at 200°, which lasted only 10 days, the diffusivity found being 0·007 and 0·008.

As the above experiments were conducted at temperatures above the melting point of the eutectic alloy of gold and lead (200°), care was taken to ascertain whether gold would diffuse in solid lead well below this point, and for this purpose the temperature chosen was 165°. The diffusivity could still be determined, and was ascertained to be 0·005 and 0·004 sq. cm. per diem in two experiments. Even at 100° the diffusion of gold in solid lead can still be determined, the diffusivity being about 0·00002, or only 1/100,000th of that which occurs in liquid lead.

Experiments were made on the diffusion of gold in solid silver at 800°, this being 160° below the melting point of silver, and 50° below that of the eutectic alloy of gold and silver. The temperature was intermittent, so that the true diffusivity could not be taken, but the diffusivity is of the same order as that of gold in lead at 200°. It would appear, therefore, that the melting points of the metals have a dominating influence on the resistance offered to diffusion.

H. C.

Relation between Osmotic Pressure and the Law of Active Masses. By ALEXANDR A. JAKOWKIN (*Zeit. physikal. Chem.*, 1896, **20**, 321—327).—Starting with Nernst's law that the active mass of a solvent is at constant temperature proportional to its vapour pressure (Abstr., 1893, ii, 367), the equation $x(a - 1 + x) = kv(1 + x)$ leads to $c/C\left(a - \frac{C - c}{C}\right) = kv(C - c)/C$, where C is the vapour pressure of the solvent and c that of the solution. From this, by neglecting the coefficient c/C , which is nearly equal to unity, the equation $PV(1 + kv) = RT$ is derived for the osmotic pressure. It is hence not exactly equal to the gas pressure, but as kv is generally very small, it is approximately so.

L. M. J.

The Course of Chemical Reactions in Gases. By ERNST COHEN (*Zeit. physikal. Chem.*, 1896, **20**, 303—306).—Storch, in a paper on this subject (this vol., ii, 296), came to the conclusion that the reaction for the formation of water from the mixed gases is not a trimolecular reaction, but one of the 9th order, obtaining a constant value for k in the equation $dc/dt = kc^9$. The author does not consider that the results justify the conclusion owing to the enormous influence of the walls of the containing vessels on the reaction velocities of gases. In the decomposition of arsenic trihydride, a constant k is not obtained until the walls of the vessel become completely covered with arsenic. During the long heating in Storch's experiments, the author considers that the velocity constant would certainly alter, so that the fact that the equation of the 9th order leads to a constant value indicates that the reaction itself cannot be of this order.

L. M. J.

The Influence of Pressure on Reaction Velocities. By VICTOR ROTHMUND (*Zeit. physikal. Chem.*, 1896, **20**, 168—179).—The experiments of Röntgen showed that at high pressures the velocity of

inversion of cane sugar is diminished, a result which he ascribed to a decrease in the dissociation of the acid. This conclusion was, however, contested by Tammann (Abstr., 1894, ii, 410). Moreover, high pressures were proved by Fanjung (Abstr., 1894, ii, 438) to cause an increase in the conductivity, although the number of ions is only very slightly altered. The author has, therefore, re-examined the effect of pressure on the velocity of inversion of cane sugar, and obtained results in complete agreement with those of Röntgen (*Ann. Phys. Chem.*, 1892, **45**, 98), the velocity decreasing by about 1 per cent. per 100 atmospheres. In order to see whether this effect is really due to a change in the number of ions, the effect of pressure on the velocity of hydrolysis of methylic and ethylic acetates was determined, hydrochloric acid of the same strength as before being employed. In this case, however, the velocity was found to *increase* to the extent of about 3.7 per cent. per 100 atmospheres. The velocity was found to be equally well represented by a linear or exponential formula, and no change was obtained when the concentration of the acid was altered, or by the use of nitric acid. From this, the author concludes that the effects cannot be due to alterations in the dissociation. If the presence of "active" and "inactive" molecules be assumed, of which only the former can undergo decomposition, the results may be explained by the effect of pressure on the equilibrium between the active and inactive molecules (Abstr., 1889, 1103). L. M. J.

New Relations between the Atomic Weights of the Elements.

By M. CAREY LEA (*Zeit. anorg. Chem.*, 1896, **12**, 249—252).—In a previous paper on the colour of atoms, ions, and molecules (Abstr., 1895, ii, 441) cerium was classed with the eleven elements whose ions are in some cases coloured, in others colourless. The author now classes cerium amongst the elements having coloured ions: the ion of the ceri-compounds is without doubt coloured; the ion of the cero-compounds appeared to be colourless, but these compounds have a faint red colour. Gold was placed in the former paper amongst the series which gives only coloured ions; there is some doubt, however, with regard to the auro-compounds. The oxides and haloids are coloured, but are insoluble, and therefore the colour of the ions cannot be determined. Aurous chloride, however, dissolves in sodium chloride and yields colourless salts, and other aurous double salts are colourless, and yield colourless solutions. The soluble aurous salts appear to be colourless, and the author, therefore, places gold amongst those elements yielding both coloured and colourless ions.

If the difference between the atomic weights of each two elements as arranged in the author's series be taken, it is found that in the first series the difference is very near to the number 16; then follow 20 elements with a difference which begins at 41.3 and gradually increases to 49. The differences between the remaining elements is 88, with the exception of that between iridium and thallium, whose atomic weights are not yet satisfactorily determined. E. C. R.

Inorganic Chemistry.

The Density of Hydrogen. By EDWARD W. MORLEY (*Zeit. physikal. Chem.*, 1896, **20**, 242—271).—Five series of determinations of the density of hydrogen were made. In the first series, the gas was weighed in large calibrated flasks, and the pressure and temperature taken by a barometric manometer and mercury thermometer. In the second series, the volume was measured at the temperature of melting ice, and the pressure measured by a siphon barometer. The details of these methods are practically the same as those in the case of the oxygen determinations (*Abstr.*, 1895, ii, 261; this vol., ii, 518). The hydrogen was obtained by electrolysis, and the utmost pains taken to ensure its purity; in those cases where analysis showed nitrogen to have been present (maximum, 0.0045 per cent.) the density was corrected for this. The results of the 15 experiments of the first series varied between $D = 0.089993$ and 0.089846 (grams/litre) with the mean value 0.089938 ± 0.000007 . The results of 19 determinations of the 2nd series varied between 0.090144 and 0.089869 with a mean value 0.089970 ± 0.000011 . In the third, fourth, and fifth series, a tube containing 600 grams of palladium charged with hydrogen was placed in communication with three exhausted calibrated flasks of a total capacity of 42 litres, kept in melting ice. The weight of the hydrogen was obtained by the loss in weight of the palladium tube, and the pressure of the gas, read by a siphon barometer; by this method, the weighing of the hydrogen is effected with greater accuracy than when it was made in the measuring flasks themselves, and the author considers this method to be far preferable to the former. Full details of the apparatus and the manipulation are given in the paper. The results of these last three series are—

	No.	Mean value.	Difference of extremes.
3rd	8 determinations	0.089886 ± 0.0000049	0.000040
4th	6 ,,	0.089880 ± 0.0000080	0.000070
5th	11 ,,	0.089866 ± 0.0000034	0.000044

The final mean of the results is given as $D = 0.089873 \pm 0.0000027$.

L. M. J.

Helium, a Gaseous Constituent of certain Minerals. Part II. Density. By WILLIAM RAMSAY (*Proc. Roy. Soc.*, 1896, **59**, 325—330; see *Abstr.*, 1895, ii, 498). The gas obtained from clèveite contains some, but not much, nitrogen, and no hydrogen. Samples of gas from bröggerite, samarskite, and fergusonite, obtained by heating the mineral in a vacuum, are rich in hydrogen; the amount of nitrogen is in all cases infinitesimal. The yield from these sources is

very variable; for whereas 1 gram of clèveite yielded 7.2 c.c. of helium, 1 gram of bröggerite yielded somewhat less than 1 c.c. of helium; the yield from samarskite was about 0.6 c.c. per gram; and from fergusonite 1.1 c.c. per gram, the last by heating alone; with the other minerals, the residue, after heating, was fused with hydrogen potassium sulphate. The gas obtained from fergusonite, on heating, was found on analysis to have the following percentage composition:—Hydrogen, 54.7; carbonic anhydride, 13.9; helium, 31.2. No hydrocarbons were present, and the residue gave a spectrum free from nitrogen flutings, even when the pressure was comparatively high.

Density determinations were made with gas purified by treatment with caustic soda, and circulation over red-hot copper oxide, soda-lime, and phosphoric anhydride. The bulb used had the capacity 162.843 c.c., and the possible error in the results may amount to 0.014. The following numbers were obtained.

		Means.
Mixture of gas from bröggerite and cleveite ..	2.218	—
Same mixture, recirculated	2.133	—
The last sample is probably the purer.		
Bröggerite gas; fresh sample	2.181	2.181
Samarskite; heat alone	2.121	2.118
Samarskite; fusion with HKSO_4	2.122	
Samarskite; gas again circulated	2.117	
Samarskite; after further circulation	2.114	
Fergusonite; heat alone	2.147	2.140
Fergusonite; another sample	2.139	
Fergusonite; another sample	2.134	

These numbers furnish some ground for the supposition that the helium from various sources is not quite homogeneous, but that different samples differ slightly in density. They point to a possible division into groups. The gas from bröggerite appears to have the density 2.18, that from samarskite 2.12, and that from fergusonite 2.14. The gas from clèveite is possibly still lighter.

The light emitted from a vacuum tube containing clèveite gas has a richer orange-yellow shade than is shown by gas from bröggerite, samarskite, or fergusonite. The cleveite gas shows, in addition to the usual strong lines, a set of fairly strong lines between the very strong green and the strong blue. These lines have never been observed in samples of gas from broggerite, samarskite, or fergusonite.

H. C.

New Gas obtained from Uraninite. By JOHN NORMAN LOCKYER (*Proc. Roy. Soc.*, 1896, 59, 342—343).—Runge and Paschen, as the result of diffusion experiments on the gas from clèveite, came to the conclusion that the gas giving the line D_3 was heavier than the gas giving the line 5015.7, but the result was not final, as the pressures were not the same. It is important for stellar classification to settle this matter, and the author has therefore made experiments in which the pressures remained the same. These clearly indicate that if a true diffusion of one constituent takes place, the component which gives D_3 is lighter than the one which gives the line at wave-

length 5015.7. This conclusion is entirely in harmony with the solar and stellar results. H. C.

Gases obtained from the Mineral Eliasite. By JOHN NORMAN LOCKYER (*Proc. Roy. Soc.*, 1895, **59**, 1—3).—Observations have been made on the gases obtained from the mineral eliasite when heated in a vacuum; in addition to lines of known gases, others have been noted, for which no origins can be traced. Many of these are probably coincident with lines in stellar and solar spectra, but there are others with which no celestial coincidences have been traced. It is important to note that all these lines do not appear in the spectrum at the same time. In the first two portions of the mineral no trace of D_3 was noted, but in the third portion examined, all coming from the same specimen, D_3 appeared as a pretty bright line. In one experiment, the products of distillation, collected in four stages, gave different spectra. The lines observed in eliasite indicate a new gas, in some way associated with those given off by clèveite and bröggerite, and the fact that D_3 is not necessarily present in the spectrum, furnishes an additional argument in favour of the view that the gas obtained from clèveite or bröggerite is complex. H. C.

New Gases obtained from Uraninite. By JOHN NORMAN LOCKYER (*Proc. Roy. Soc.*, 1895, **59**, 4—8; compare Abstr., 1895, ii, 430 and 470).—The author in this paper brings together the notes which he has previously made on the spectra of the new mineral gases. Besides the hydrogen lines, all three chromospheric lines in Young's list which have a frequency of 100 have now been recorded in the spectra of the new gas or gases obtained from minerals by the distillation method. Determinations of the wave-lengths of many other lines in the spectra of the new gases have been made, and the results leave little doubt as to the coincidence of several lines with those appearing in the chromosphere, nebulae, and white stars. It seems very probable also that many lines which have been noted, and for which no origins have yet been traced, belong to gases which have not hitherto been recorded in the chromosphere. A table is given which summarises the chief lines which have so far been recorded in the new gases from various minerals. H. C.

Expansion of Argon and of Helium as compared with that of Air and Hydrogen. By J. P. KUENEN and WYATT W. RANDALL (*Proc. Roy. Soc.*, 1896, **59**, 60—65).—The authors have compared the readings shown by thermometers containing respectively argon, helium, hydrogen, and air, at the temperatures of the melting point of ice and the boiling points of water, chlorobenzene, aniline, quinoline, and bromonaphthalene. The helium used was of density 2.13 ($O = 16$), and the argon, which was prepared from atmospheric air by the magnesium method, had the density 19.99.

The results of the observations are given in the table. In three cases (3, 4, and 6) the reading was taken at 0° , as well as at the boiling point of water, so that the coefficient of expansion could be calculated between these two points. The higher temperatures deter-

mined have been derived from the observed pressures by using the coefficients thus measured; with the hydrogen thermometer, 0.003663 was taken as the coefficient of the gas.

Thermo- meter.	Cor- rected pressure, 0°.	In steam at about 100°	Coeffi- cient of expan- sion, 0—100°.	Temperatures calculated.			
				Chloro- benzene.	Aniline.	Quino- line.	Bromo- naphtha- lene.
1. Hydrogen.	—	712.56	—	131.6	183.9	236.35	—
2. Air I	—	737.74	—	131.8	183.6	[234.9]	281.65
3. Helium...	567.02	775.18	0.003665	132.2	184.1	236.9	[278.3]
4. Argon I..	517.02	706.06	0.003668	132.15	184.1	—	—
5. Argon II.	529.54	—	—	—	—	237.8	281.5
6. Air II....	511.68	698.79	0.003663	—	—	237.1	—

Although the authors do not claim any remarkable accuracy for these results, they serve to show that the behaviour of argon and helium, as far as expansion is concerned, and within the limits of temperature used, is the same as that of so-called perfect gases or mixtures of them.

H. C.

Some Physical Properties of Argon and Helium. By LORD RAYLEIGH (*Proc. Roy. Soc.*, 1896, **59**, 198—208).—The density of argon prepared by the aid of magnesium was found by Ramsay (this vol., ii, 99) to have a mean value of 19.941 ($O = 16$). To further test the identity of the gases, the author has determined the density of argon prepared by Cavendish's oxygen method; large scale weighings of pure argon with the globe of 1800 c.c. capacity employed in former weighings of gases, being undertaken. A series of weighings was obtained with intermediate sparkings, so as to obtain evidence that the purification had really reached a limit. The density thus determined was found to be 19.940, and the conclusion from the spectroscopic evidence that the gases, isolated from the atmosphere by magnesium and by oxygen, are essentially the same, is confirmed.

The refractivity of argon was determined in the hope that it might throw some light on the character of the gas. As absolute measurements were not required, it sufficed to compare the pressures necessary in two columns of air and argon of equal lengths, in order to balance the retardations undergone by light in traversing them. The ratio of the refractivity of argon to that of air was thus found to be 0.961, so that the evidence from the refractivities is very unfavourable to the view that argon is an allotropic form of nitrogen such as would be denoted by N_3 .

Similar comparisons were made between air and helium. The observations were not made under ideal conditions, on account of the smallness of the changes of air pressure; but, with considerable approximation, the refractivity of helium to that of air is 0.146. The

lowest refractivity previously known is that of hydrogen, nearly 0.5 of that of air.

The viscosity of argon and helium was investigated by the method of passage through capillary tubes. If the driving pressure ($p_1 - p_2$) is not too great, the volume V_2 delivered in time t through a tube of radius R and length λ is given by

$$V_2 = \pi t \frac{p_1^2 - p_2^2}{2p_2} \frac{R^4}{8\eta\lambda},$$

the volume being measured at the lower pressure p_2 , and η denoting the viscosity of the gas. The results referred to dry air were, for helium, 0.96, and for argon, 1.21, somewhat higher than for oxygen, which at present stands at the head of the list of the principal gases.

Examination of the gas from the Bath springs showed that this gas contains appreciable quantities of helium in addition to the argon already proved to be present. The gas from the Buxton springs contains about 2 per cent. by volume of argon, but the presence of helium could not be confirmed.

The question of the presence of helium in the atmosphere is, apart from its independent interest, of importance in connection with the density of atmospheric argon. Since the spectrum of this gas does not show the line D_3 , we may probably conclude that the proportion of helium is less than 3 per cent.; so that there would be less than 3×10^{-4} of helium in the atmosphere. Ramsay has shown that the solubility of helium in water is less than one-fifth that of argon, so that if a mixture of helium and argon be dissolved in water until there is only a small fraction remaining over, the proportion of helium will be much increased in the residue. 60 c.c. of argon was therefore treated with boiled water until the volume was reduced to 1.5 c.c. The gas still gave no sign of the D_3 line, and if helium is present in the atmosphere, it must be in very small quantity, probably much less than a ten-thousandth part.

H. C.

Acids containing Sulphur and Nitrogen. By MAX WAGNER (*Zeit. physikal. Chem.*, 1896, **20**, 334).—The author regrets having, in his previous paper on acids containing sulphur and nitrogen (this vol., i, 470), omitted reference to the work of Hantzsch (this vol., ii, 95, 96) and of Divers (*Ber.*, **28**, 996; **27**, 567. See *Trans.*, 1895, 452, 1095, 1098).
L. M. J.

Nitrosodisulphonic acid. By PAUL SABATIER (*Compt. rend.*, 1896, **122**, 1479—1482 and 1537—1539).—The absorption spectrum of the blue-violet solution formed by a nitrite and cuprous oxide in presence of sulphuric acid (this vol., ii, 622) is quite different from the spectra of the ammonio-cupric compounds or the purple cupric hydrobromide, but is similar to that of the deep blue-violet solution of the potassium nitrosodisulphonate described by Fremy and by Raschig.

In many cases when nitric acid or nitrogen oxides are dissolved in sulphuric acid containing sulphurous anhydride, and the solution is exposed to moist air, there are indications of the formation of a dark

blue compound. If a mixture corresponding with $2\text{NO} + \text{O}$ is passed into sulphuric acid saturated with sulphurous anhydride and cooled at 0° , the liquid remains colourless, but, on adding water very slowly, a dark blue product is formed. When a mixture of air and nitric oxide is passed into sulphuric acid of the composition $\text{H}_2\text{SO}_4 + \text{H}_2\text{O}$, saturated with sulphurous anhydride and cooled at 0° , the blue-violet compound is formed at once, with vigorous effervescence. With somewhat stronger acid, the liquid is at first colourless, but the blue-violet substance forms gradually. The reaction takes place in two stages, $2\text{NO} + \text{O} + 2\text{SO}_2 + \text{H}_2\text{O} = 2\text{NO}\cdot\text{SO}_3\text{H}$ and $2\text{NO}\cdot\text{SO}_3\text{H} = \text{NO} + \text{NO}(\text{SO}_3\text{H})_2$. Nitrosodisulphonic acid decomposes spontaneously into sulphuric acid, sulphurous anhydride, and nitric oxide, but is much more stable than the potassium salt described by Fremy, and does not decompose rapidly even at 100° .

When agitated with air or mixed with hydrogen peroxide, persulphuric acid, nitric acid, chlorine, or potassium chlorate, it is rapidly decolorised. Potassium perchlorate and bromine act more slowly. Alkali chlorides are immediately decomposed with evolution of hydrogen chloride and chlorine; potassium iodide at once decolorises the liquid, and iodine is liberated. Sulphurous acid is without action; water at once decomposes the blue compound.

Most metallic oxides and carbonates decompose the solution of nitrosodisulphonic acid, and are converted into sulphates. Ferric oxide, however, gives a wine-red solution, and the same compound is formed by placing metallic iron or a concentrated solution of ferrous chloride or sulphate, or some particles of ferrous oxalate into the acid. Ferric salts do not give this coloration.

Cupric carbonate, oxide, or hydroxide, metallic copper, or any cuprous salt yields an intense blue-violet coloration (*loc. cit.*). With copper or cuprous salts, nitric oxide is liberated. Chromic hydroxide also yields a very deep blue-violet solution, but chromium and chromous salts have no action.

In all these cases, the colour of the solutions of the salts is very much more intense than that of the acid, and the solutions themselves are more stable.

C. H. B.

Action of Silicon on Metals. By EMILE VIGOUROUX (*Compt. rend.*, 1896, 123, 115—118; compare Moissan, this vol., ii, 173).—As regards their action with silicon, the metals may be divided into two classes.

I. Those which do not combine directly with silicon, even in the electric furnace. Examples: alkali metals, zinc, aluminium, lead, tin, antimony, bismuth, gold, and silver. These all dissolve silicon to some extent, but deposit it again, in a crystalline form, on cooling.

II. Those which combine directly with silicon to form crystalline silicides. Examples: iron, chromium, nickel, cobalt, manganese, copper and platinum.

Platinum silicide, SiPt_2 , is a white, extremely hard, brittle solid, its sp. gr. at 18° is 13.8, it is capable of dissolving silicon, and is attacked, when hot, by chlorine and by aqua regia.

J. J. S.

Diamonds from Steel. By A. ROSSEL (*Compt. rend.*, 1896, 123, 113—115; compare Moissan, *Abstr.*, 1893, ii, 275; 1894, ii, 189).—Small diamonds have been obtained from hard steels produced at high temperatures and cooled under great pressure. The steels were treated according to the methods recommended by Berthelot (*Ann. Chim. Phys.*, [4], 19, 392), and by Moissan (*loc. cit.*).

The crystals have the same form, appearance, and properties as those described by Moissan. J. J. S.

Action of Zinc on the Photographic Plate. By R. COLSON (*Compt. rend.*, 1896, 123, 49—51).—The author shows that if a piece of zinc foil, which has been kept for some time, be partially rubbed with emery paper and then placed in contact with a gelatino-bromide plate for some 24 hours, the plate on development takes on a deep grey tint where the recently rubbed zinc rested, a lighter grey tint where the bright but not recently rubbed surface rested, and that scarcely any change at all is noticeable where the oxidised surface of the zinc came in contact with the plate. This action is due to minute traces of zinc vapour which are given off at ordinary temperature and pressure from a freshly polished zinc surface; the emanation of vapour, however, diminishes as the surface becomes oxidised.

The image is only formed after development, and the author thinks that in certain cases the light used in photography may be replaced by polished zinc-foil.

The zinc vapour has the power of penetrating all porous substances, such as paper, thin strips of wood, &c. Compact substances are opaque to the vapour.

Magnesium and cadmium have the same action on a gelatino-bromide plate, but not lead, tin, copper, iron, or aluminium.

J. J. S.

Vaporisation of Metals at the Ordinary Temperature. By HENRI PELLAT (*Compt. rend.*, 1896, 123, 104—105; compare Colson, preceding abstract).—Experiments made by the author some four years ago show that steel has an action on a photographic plate even when separated from it by a sheet of cardboard. The steel used was in the form of a magnetised bar, the exposure varied from 15 days to several months, and all precautions were taken to exclude light. The action is attributed to the vaporisation of the steel at ordinary temperatures, and to the passage of the vapour through the cardboard.

J. J. S.

Preparation of Alloys. By HENRI MOISSAN (*Compt. rend.*, 1896, 122, 1302—1303).—Many alloys can be obtained by taking advantage of the ease with which metallic oxides are reduced by aluminium. The general method is to throw a mixture of aluminium filings and the oxide of the particular metal into melted aluminium. Part of the aluminium burns, and there is such an energetic development of heat that the most refractory oxides are reduced, the metal mixing with the excess of aluminium. In this way alloys of aluminium with

nickel, molybdenum, tungsten, uranium, and titanium, have been prepared. An alloy can be obtained containing as much as 75 per cent. of tungsten.

The direct preparation of a copper-chromium alloy is difficult, but an aluminium-chromium alloy is readily obtained in the manner indicated, and this dissolves in all proportions in fused copper forming a copper-aluminium-chromium alloy, from which the aluminium is readily eliminated by stirring in cupric oxide, a copper-chromium alloy being left. A similar method can be applied to the introduction of tungsten and titanium into Siemens-Martin steel. C. H. B.

Fusibility of Metallic Alloys. By HENRI GAUTIER (*Compt. rend.*, 1896, 123, 109—113).—Fused alloys, on solidification, behave in a similar manner to fused mixtures of salts, and hence may be divided into three classes corresponding with the three classes of saline mixtures recognised by Le Chatelier.

(1) The metals do not combine in any fixed proportions, and the two constituents crystallise quite distinctly; for example, alloys of tin with zinc, bismuth, or lead.

(2) A definite compound of the two metals crystallises out, but these crystals are scattered in a crystalline matrix of the metal which is in excess; for example, copper with tin or antimony.

(3) Alloys corresponding with isomorphous mixtures of salts; for example, gold with silver.

The fusibility curve of an alloy at once indicates to which of these three classes the alloy belongs.

The author has studied the fusibility of four alloys, tin-nickel, tin-aluminium, aluminium-silver, and antimony-aluminium, and the results show that all four alloys belong to the second class. The curves indicate the following definite compounds, Ni_3Sn_2 , SnAl , or Sn_3Al_2 , Ag_2Al , and SbAl .

Of antimony-aluminium alloys, all which contain more than 2 per cent. of antimony are less fusible than aluminium, and thus form an exception to the rule that binary alloys fuse more readily than the less fusible constituent. Antimony-aluminium alloys, which approximate in composition to SbAl , have the curious property of being slowly and spontaneously reduced to a powder, and the powder thus formed does not melt below 1100° , although the least fusible of these alloys melts at 1050° . The author gives the melting point of antimony, as determined by the pyrometer, as 632° , and not 430° , as stated in text-books. J. J. S.

Action of Phosphorus on Metallic Chlorides. By A. GRANGER (*Compt. rend.*, 1896, 122, 1484—1485).—Phosphorus vapour at a low red heat converts nickel and cobalt chlorides into the corresponding sesquiphosphides Ni_2P_3 and Co_2P_3 . The former is grey, very friable, has a graphitic lustre, and a crystalline and schistose structure, whilst the latter is black, has a metallic lustre, and is readily powdered. These sesquiphosphides are not magnetic; they are not attacked by hydrochloric or nitric acid, or by aqua regia, and chlorine begins to decompose them only at the melting point of hard

glass. They do not alter on exposure to air at a dull red heat, but lose phosphorus when heated in a blow-pipe flame.

Mercuric, stannic, and cadmium chlorides are not affected by phosphorus vapour under similar conditions, and gold and silver chlorides are reduced to the metallic state. Cupric chloride is reduced to cuprous chloride, and eventually yields copper diphosphide if the temperature is below dull redness; at a higher temperature, the composition of the crystalline product is not constant but varies between CuP_2 and Cu_2P_2 . C. H. B.

Action of High Temperatures on certain Sulphides. By A. MOURLOT (*Compt. rend.*, 1896, **123**, 54—57).—Amorphous lead sulphide, when heated in the electric furnace for eight minutes with a current of 35 volts and 50 ampères, yields crystals of galena; when heated for 40 minutes, a mixture of galena and metallic lead is obtained, and with stronger currents, metallic lead alone.

Antimony sulphide behaves in a similar manner, yielding stibnite and the metal; with a current of 300 ampères and 60 volts, however, it is completely desulphurised in a few minutes.

Amorphous zinc sulphide yields würtzite, cadmium sulphide yields greenockite, and aluminium sulphide forms a crystallised variety when similarly treated. J. J. S.

Desilverisation of Lead by Electrolysis. By DONATO TOMMASI (*Compt. rend.*, 1896, **122**, 1476—1477).—The argentiferous lead is cast into convenient forms, and is made the anode in a solution of lead sodium acetate, or lead potassium acetate, which has a very low resistance, and does not yield any lead peroxide on electrolysis. The cathode is a disc of some metal which is not attacked by the liquid; the general arrangement of the electrolytic cell has previously been described (this vol., ii, 511). When the circuit is complete, the lead is transferred from the anodes to the cathode in a spongy form which is readily removed from time to time, whilst the silver falls into a perforated receiver placed below the anode. The lead is afterwards fused with charcoal and the silver with sodium nitrate and borax. C. H. B.

Aluminium Alloys. By CHARLES COMBES (*Compt. rend.*, 1896, **122**, 1482—1484).—When aluminium alloys are prepared by adding a mixture of a metallic oxide and aluminium powder to fused aluminium as proposed by Moissan (this vol., ii, 601), there is loss of aluminium and the alumina which is formed does not separate readily from the alloy. Better results are obtained by adding the sulphide or chloride of the particular metal to the fused aluminium; in the first case the aluminium sulphide rises to the surface of the metal, in the second the aluminium chloride volatilises. Metallic sulphides can be employed when the heat of formation is lower than that of aluminium sulphide; the chlorides can often be used even when their heat of formation is somewhat higher than that of aluminium chloride. When sulphides are used, part of the sodium that is often present in aluminium is eliminated in the sulphide formed.

Aluminium-nickel alloys containing 20 per cent. of nickel were prepared by means of the sulphide; aluminium-manganese alloys containing 4 per cent. of manganese were prepared by means of anhydrous manganous chloride, and have a crystalline fracture resembling that of spiegeleisen. Aluminium-chromium alloys were obtained by using chromic chloride; one containing 7 per cent. of chromium is very brittle, and has a finely crystalline structure, whilst another containing 13 per cent. of chromium is completely crystalline and can be powdered in a mortar. C. H. B.

Hydrolytic Decomposition of Ferric Nitrate and Sulphate.

By UBALDO ANTONY and G. GIGLI (*Gazzetta*, 1896, 26, i, 293—311).—The authors have examined ferric nitrate and sulphate by methods similar to those which they used with ferric chloride (this vol., ii, 250).

On evaporating concentrated ferric nitrate solution, in which the dissolved matter has the composition $\text{Fe}(\text{NO}_3)_3$, at ordinary temperatures, nitric acid is given off. The dissociation of pure ferric nitrate in aqueous solutions, just as in the case of the chloride, increases with the dilution and also with the time elapsing since the preparation of the solution. The salt in the more dilute solutions becomes completely dissociated after a time into colloidal ferric hydroxide and nitric acid, as is shown by the facts that sodium chloride precipitates ferric hydroxide, and that potassium ferrocyanide gives no blue coloration in such solutions; in less dilute solutions, to which ferrocyanide has been added, the blue colour gradually increases in intensity owing to the continued re-formation of the ferric nitrate. Aqueous solutions of ferric nitrate containing less than 0.1 per cent. are quite colourless, thus differing from other dilute solutions of ferric salts which are always coloured; it is supposed that in such dilute ferric nitrate solutions, basic ferric salts are not formed, but rather salts of pyronitric acid, $\text{H}_2\text{N}_2\text{O}_7$, or orthonitric acid H_3NO_5 . Ferric orthonitrate and pyronitrate being simply products of hydrolysis of ferric nitrate, the reaction between all three salts and water is a reversible one; the orthonitrate by further hydrolysis dissociates into ferric hydroxide and nitric acid. Although differing in a few respects, ferric nitrate and ferric chloride solutions behave on the whole very similarly on dilution; solutions of ferric sulphate, however, behave dissimilarly to these two. Clear neutral ferric sulphate solution remains clear until highly diluted, when it becomes gradually turbid owing to deposition of ferric hydroxide; ferric sulphate thus undergoes hydrolytic dissociation in aqueous solution and the dissociation becomes complete in solutions of about 1 in 60,000, sulphuric acid and non-colloidal ferric hydroxide being formed. During the decomposition, true basic ferric salts are first formed and ultimately converted into insoluble ferric hydroxide. The ferric sulphate is slowly reformed on disturbing the equilibrium by adding potassium ferrocyanide if the solution be not too dilute to allow of the solution of the ferric hydroxide in the sulphuric acid.

The amounts of water necessary to decompose equivalent quantities of ferric chloride, nitrate, and sulphate are approximately in

the ratio of the avidity constants of the three acids; the slight divergence in the case of the sulphate being attributed to the fact that the ferric hydroxide does not remain colloidal in presence of sulphuric acid. W. J. P.

Compounds of the Lower Oxides and Sulphides of Molybdenum with Ammonia and with Potassium Cyanide. By K. VON DER HEIDE and KARL A. HOFMANN (*Zeit. anorg. Chem.*, 1896, **12**, 277—292).—The compound $4\text{MoO}_3, \text{MoO}_2, 2\text{NH}_3 + 7\text{H}_2\text{O}$ is obtained by heating an aqueous solution of ammonium molybdate with half its weight of hydroxylamine hydrochloride on the water bath until the orange precipitate which is at first formed is dissolved, and a greenish-brown solution is obtained; this solution is then rapidly filtered, protected from access of air, and allowed to cool. The compound separates in dark red crystals belonging to the triclinic system, dissolves gradually in water with a reddish-yellow coloration, and is fairly stable. It gradually reduces Fehling's solution in the cold and quickly when heated. With copper sulphate, it gives a beautiful, blue coloration; with mercurous and mercuric salts, a flesh coloured precipitate; with lead nitrate, a yellowish-white precipitate; and with potassium thiocyanate, an intense red coloration. It is gradually decomposed by dilute acids, and reduces ammoniacal silver solution with separation of metallic silver. The authors were unable to obtain other ammonia derivatives with the lower oxides of molybdenum, analogous to the chromamine bases.

The compound $\text{MoO}_2, 4\text{KCN}, \text{NH}_2\cdot\text{OH} + \text{H}_2\text{O}$ is obtained on heating a solution of molybdic acid (10 grams) in an excess of potassium hydroxide with potassium cyanide (20 grams) and hydroxylamine hydrochloride (5 grams); nitrogen is evolved, and the heating is continued until a reddish-violet solution is obtained. On cooling, the compound crystallises in beautiful, violet, monoclinic forms, the aqueous solution of which is red, and shows a characteristic absorption in the green. Yellow oxidation products are gradually formed on exposure to the air. The compound is decomposed by dilute acids with an intense red coloration, and evolution of hydrogen cyanide. It is easily decomposed by strong reducing agents, sodium amalgam, or excess of hydroxylamine, and gives precipitates with mercury, lead, and iron salts. It is not altered by yellow ammonium sulphide in the cold, and, on heating, yields molybdenum trisulphide.

The compound $\text{MoO}_2, 4\text{KCN} + 10\text{H}_2\text{O}$ is obtained as follows: molybdenum trioxide is treated with potassium iodide and hydrochloric acid, and the liberated iodine eliminated by steam distillation; the greater portion of the hydrochloric acid is then removed by evaporation, and the solution neutralised with potassium hydroxide, and mixed with a concentrated solution of potassium cyanide. As soon as the solution changes to a beautiful blue, a large excess of potassium hydroxide is added, whereby the compound is precipitated. It crystallises in bluish-red tablets belonging to the rhombic system; $a : b : c = 0.7324 : 1 : 0.5723$. It is not decomposed by cold dilute acids, but with concentrated sulphuric acid, it gives a black precipitate insoluble in ammonia, and it is decomposed by concentrated hydro-

chloric and nitric acids without the formation of a precipitate. With silver nitrate, it yields a black precipitate, which, on treatment with nitric acid, is converted into silver cyanide. It gives a green coloration with ammonium sulphide, and, on heating, yields sulphomolybdate. With thiocyanates in acid solution, it yields a red compound, which can be extracted by shaking with ether. On precipitating with alcohol the blue mother liquors obtained in the preparation of this salt, and crystallising the precipitate from a small quantity of water, bright, greenish-blue plates were obtained of the formula



and a further crystallisation of the mother liquors yielded compounds which, on analysis, gave numbers agreeing with the formulæ $\text{MoO}_2\text{CN}, 3\text{KCN} + \text{H}_2\text{O}$; $\text{MoO}_2\text{CN}, 3\text{KCN}$, and $\text{MoO}_2, 3\text{KCN} + 4\text{H}_2\text{O}$.

Hydrated molybdenum bisulphide dissolves in potassium cyanide to an intensely green solution, and, on adding alcohol, a greenish oil is precipitated, which gradually solidifies. According to the length of time which is allowed for the action of the potassium cyanide, three different compounds are obtained.

The compound $\text{Mo}_2\text{S}_3, 6\text{KCN} + 5\text{H}_2\text{O}$ is obtained by a mild action of the cyanide for a short time. It crystallises in green needles having a silky lustre, is easily soluble in water, and is not altered by alkalis, but is gradually decomposed by dilute mineral acids. It yields characteristic precipitates with mercury, copper, silver, and ferric salts. When warmed with ammonium sulphide, a thiomolybdate is formed.

The compound $\text{Mo}_2\text{SO}(\text{CN})_2, 4\text{KCN} + 4\text{H}_2\text{O}$ is obtained by evaporating the solution of the bisulphide in potassium cyanide in a vacuum at the ordinary temperature. It crystallises in beautiful, reddish-brown needles, easily soluble in water; it is stable towards dilute acids and alkalis, but is decomposed by boiling with hydroxylamine with the formation of a red precipitate.

The compound $\text{Mo}_3\text{S}_4(\text{CN})_3, 5\text{KCN} + 7\text{H}_2\text{O}$ is obtained by allowing the preceding salt to remain in contact with the mother liquor over sulphuric acid. It separates in large crystals resembling black augite, and appears green by transmitted light. It gives a green solution in water, is not altered by dilute acids or alkalis in the cold, yields a thiomolybdate when warmed with ammonium sulphide, and gives precipitates with copper, lead, and mercury salts. With silver nitrate, it yields a blackish-brown precipitate, which is converted into silver cyanide when treated with nitric acid. E. C. R.

Researches on Tungsten. By HENRI MOISSAN (*Compt. rend.*, 1896, 123, 13—16; compare *Abstr.*, 1893, ii, 471).—Tungsten, in a state of purity, may readily be obtained by heating a mixture of tungstic acid (800 grams) with sugar carbon (80 grams) in the electric furnace, the heating being continued for 10 minutes with a current of 900 amperes and 50 volts. A residue is left which, although distinctly molten on the surface, is quite porous internally.

If the complete fusion of the metal is avoided, the carbon of the crucible does not take part in the reaction, and the excess of tungstic acid is volatilised. The metal, as thus obtained, contains no carbon

and is very pure. In the porous state it can be welded like iron; it can also be filed easily, and, when free from carbon, will not scratch glass. When heated with carbon, as in the cementation process, the exterior portions contain carbon, and become hard enough to scratch rubies.

Pure tungsten is less fusible than chromium or molybdenum; it has a sp. gr. = 18·7, and has no action on a magnetised needle.

Fluorine attacks the metal at the ordinary temperature with incandescence, and yields a volatile fluoride; neither nitrogen nor phosphorus has any action on tungsten at a red heat. Silicon and boron, if heated in the electric furnace with tungsten, yield crystalline compounds of metallic lustre, which are capable of scratching rubies. At 1200°, carbonic anhydride is reduced by tungsten, yielding the blue oxide, but no carbon is deposited. The metal is not readily acted on by moist air, but is slowly attacked by water containing carbonic anhydride. Sulphuric, hydrochloric, and hydrofluoric acids act but slowly, whereas a mixture of hydrofluoric and nitric acids dissolves the metal readily. Oxidising agents, such as lead dioxide and potassium chlorate, readily act on the powdered metal.

If, in the preparation of tungsten, the heating is continued for a longer time, the metal melts and combines with the carbon of the crucible. With an excess of carbon, the metal readily forms a definite *carbide*, CW_2 ; this is iron-grey, is harder than corundum, and at 18° has a sp. gr. = 16·06; it has much the same properties as the metal, but is, as a rule, more readily acted on. Boiling nitric acid readily dissolves the carbide, whereas other acids act but slowly.

J. J. S.

Zirconotungstic Compounds. By L. A. HALLOPEAU (*Compt. rend.*, 1896, 122, 1419—1422).—Gelatinous zirconium oxide, prepared by the action of potassium hydroxide on potassium fluorozirconate, dissolves in a boiling solution of potassium paratungstate,



and yields a *zirconodecatungstate*, $10\text{WO}_3, \text{ZrO}_2, 4\text{K}_2\text{O} + 15\text{H}_2\text{O}$; this separates from boiling water in small crystals, which act feebly on polarised light. The mother liquor of this salt, when concentrated in a vacuum, yields a *dizirconodecatungstate*, $10\text{WO}_3, 2\text{ZrO}_2, 4\text{K}_2\text{O} + 20\text{H}_2\text{O}$, in very small, prismatic crystals, which act strongly on polarised light, and show extinction at 30° from the axis of elongation. Both these compounds are almost insoluble in cold water, are converted into insoluble compounds when heated, and yield a mixture of tungstate and zirconate when fused with alkali carbonates. In general properties, they resemble the silicotungstates; the zirconodecatungstate is analogous in composition to the silicodecatungstate, except that it contains a somewhat smaller proportion of water.

Ammonium zirconodecatungstate, $10\text{WO}_3, \text{ZrO}_2, 3(\text{NH}_4)_2\text{O}, \text{H}_2\text{O} + 13\text{H}_2\text{O}$, is obtained in a similar way, and forms small, rhomboidal prisms, which act strongly on polarised light and show extinction parallel with the axes. The crystals lose water even in contact with the liquid in which they are formed.

The zirconodecatungstates are immediately decomposed by nitric, hydrochloric, or sulphuric acid, with precipitation of tungstic acid, and acetic acid behaves in a similar manner. Phosphoric acid precipitates gelatinous zirconium phosphate. Ammonia precipitates zirconium hydroxide, and the precipitate does not redissolve when the liquid is boiled and the ammonia expelled. In the case of the silico-decatungstates, the precipitate redissolves. Potassium hydroxide produces a similar precipitate, and the salts of many metals precipitate insoluble zirconodecatungstates.

C. H. B.

Action of Iodine on Stannous Chloride. By V. THOMAS (*Compt. rend.*, 1896, 122, 1539—1541).—When iodine is added to stannous chloride in presence of carbon bisulphide, the liquid is at first rapidly decolorised, and, in the end, remains orange-red. If the bisulphide, in which stannous chloride is quite insoluble, is decanted off and distilled, it is found to contain stannic iodide and iodine trichloride; these can be separated by heating at 150—200°, when the latter volatilises and the iodide is left in a well crystallised form. No stannic chloridide is obtained, and the reaction seems to be represented by the equation $3\text{SnCl}_2 + 7\text{I}_2 = 3\text{SnI}_4 + 2\text{ICl}_3$.

C. H. B.

Vanadium and Vanadium Carbide. By HENRI MOISSAN (*Compt. rend.*, 1896, 122, 1297—1302).—Vanadic anhydride (182 grams), mixed with sugar carbon (60 grams), in quantities of 300 grams at a time, is heated for 5 minutes in the electric furnace with a current of 900 ampères and 50 volts. In this way, vanadium is obtained containing 10.5 to 16.2 per cent. of carbon, but if the proportion of sugar carbon amounts to one-fifth of the vanadic anhydride, the reduced vanadium contains 9.2 to 9.9 per cent. of carbon (compare Abstr., 1893, ii, 471). The volatility of the vanadic anhydride makes its reduction difficult, and likewise interferes with the subsequent purification of the vanadium. However, by heating vanadic anhydride for two minutes only in an atmosphere of hydrogen in a carbon tube in the electric furnace with a current of 1,000 ampères and 60 volts, the reduced metal contains only 4.4 to 5.3 per cent. of carbon. It is then white, has a brilliant lustrous fracture, and does not alter when exposed to air; sp. gr. = 5.8 at 20°. It burns in oxygen at a red heat, and is attacked by chlorine at dull redness, but does not become incandescent, and combines readily with nitrogen. It is not affected by hydrochloric acid, and only very slowly by boiling concentrated sulphuric acid.

If the mixture of vanadic anhydride and carbon is heated in the carbon tube of the electric furnace for 9 or 10 minutes, *vanadium carbide* is obtained; this has the composition VC, forms distinct crystals, scratches quartz, melts at a temperature somewhat above the melting point of molybdenum, and is volatile; its sp. gr. is 5.36. It becomes incandescent if heated in chlorine above 500°, burns vigorously in oxygen at a dull-red heat, but does not combine with sulphur at the melting point of glass, and does not react with hydrogen chloride, water vapour, or hydrogen sulphide at dull redness.

Nitrogen and ammonia attack it readily at a red heat, with formation of a nitride. Sulphuric and hydrochloric acids have no action on it, but it is attacked by nitric acid in the cold, and is oxidised readily by fused potassium nitrate or chlorate.

Vanadium, notwithstanding its high melting point, readily forms alloys. A mixture of ferric oxide, vanadic anhydride, and sugar carbon, when heated in the electric furnace, yields a greyish-white, crystalline, brittle alloy containing nearly 20 per cent. of vanadium, and about 8 per cent. of carbon. With copper oxide in place of ferric oxide, an alloy containing 96.52 per cent. of copper and 3.38 per cent. of vanadium is obtained; it is very malleable, is easily filed, and is harder than copper. An alloy of aluminium with 2.5 per cent. of vanadium is obtained by throwing a mixture of vanadic anhydride and aluminium filings into fused aluminium; it is very malleable, but too soft to be filed readily. Silver and vanadium do not form an alloy.

C. H. B.

Action of Nitric Peroxide on Antimony Trichloride. By V. THOMAS (*Compt. rend.*, 1896, 123, 51—54; compare Abstr., 1895, ii, 450).—Antimony trichloride absorbs but little nitric peroxide in the cold, but at its melting point it readily absorbs the gas, becoming first pale yellow, then dark, and finally red. If slowly cooled, it still retains a yellow colour, and contains a certain quantity of the peroxide; it loses the gas, however, when placed in a vacuum or when left exposed for some time to dry air. The question as to whether the peroxide is chemically combined with the chloride or only exists in a state of solution, has been settled by the author by determining the vapour tension of the gas evolved at given temperatures. If a definite compound exists, then it must dissociate at the ordinary temperature, and, according to the laws of dissociation, the tension should remain constant for a given temperature. It was impossible to measure the vapour tension directly on account of the action of nitric peroxide on mercury, but it was accomplished indirectly by estimating the amount of peroxide present in a known volume of the mixed gases by absorbing the peroxide with dilute alkali, and titrating the nitrite formed with potassium permanganate. The vapour tension varied from 3 mm. to 491 mm. for the same temperature (22.5°), thus indicating that the peroxide forms no definite compound with antimony trichloride, but simply remains dissolved.

J. J. S.

Solubility of Carbon in Rhodium, Iridium, and Palladium.

By HENRI MOISSAN (*Compt. rend.*, 1896, 123, 16—18; compare Abstr., 1893, ii, 320).—Rhodium, when heated in the electric furnace in the presence of carbon, takes up a small quantity of the latter. With a current of 300 ampères and 50 volts, 1.42 per cent. of carbon was dissolved; with a current of 910 ampères and 50 volts acting during 5 minutes, a larger quantity of carbon, 2.72—7.38 per cent., was absorbed. The greater the amount of carbon the metal contains, the less malleable it becomes; this carbon is left behind in the form of graphite when the metal is heated and chlorine is passed over it.

Iridium and palladium react in a similar manner, dissolving carbon at the temperature of the electric furnace, but yielding it up again, before they solidify, in the form of crystals of graphite.

J. J. S.

Mineralogical Chemistry.

Reproduction of Sodium Magnesium Chlorocarbonate, Sodium Magnesium Carbonate, Darapskite, and Hydrargillite.

By AUGUST B. DE SCHULTEN (*Compt. rend.*, 1896, 122, 1427—1429).—Sodium magnesium chlorocarbonate is obtained by heating 150 grams of sodium chloride, 20 grams of sodium carbonate (anhydrous), and 15 grams of magnesium chloride with 550 c.c. of water in a closed flask for eight hours at 100°; it separates in regular octahedra of the composition $\text{Na}_2\text{CO}_3, \text{MgCO}_3, \text{NaCl}$; sp. gr. = 2.377 at 15°. It is decomposed by cold water, and melts and decomposes at a red heat.

The double carbonate is obtained by reducing the proportion of sodium chloride and increasing that of the carbonate. A good method is to mix a solution of 20 grams of crystallised magnesium nitrate in 50 c.c. of water with a solution of 100 grams of anhydrous sodium carbonate in 400 c.c. of water, and heat the mixture in a closed flask at 100° for 4—5 hours; it crystallises in flat rhombohedra of the composition $\text{Na}_2\text{CO}_3, \text{MgCO}_3$, the acute angle of the face p being about 73°; sp. gr. = 2.729 at 15°.

Artificial darapskite, $\text{NaNO}_3, \text{Na}_2\text{SO}_4, \text{H}_2\text{O}$, is obtained by dissolving 250 grams of crystallised sodium sulphate in 500 grams of water, adding 400 grams of sodium nitrate, and allowing the filtered liquid to cool slowly. The crystals do not alter at the ordinary temperature but lose water slowly at 100°; sp. gr. = 2.197 at 15°; they are monoclinic, elongated along h' , showing the faces $p(001)$, $g'(010)$, $m(110)$, $o'(101)$, $o^1(302)$, $a^1(201)$, the angles being $h'p$ 76° 50', $h'm$ 56° 0', $h'o$ 54° 0', $h'o^1$ 44° 50', and $h'a^1$ 52° 50', which are practically identical with those of the natural mineral.

Hydrargillite (gibbsite) is obtained in distinct crystals by precipitating aluminium hydroxide from a very dilute ammoniacal solution, and heating on a water bath for 15 days. Better results are obtained by slowly precipitating the hydroxide from a hot alkaline solution by means of carbonic anhydride. The crystals contain a small quantity of silica; sp. gr. = 2.423. They show the faces $p(001)$, $h'(100)$, and $m(110)$: the angles $h'm$ and mm are very nearly 120°, and in crystals macled along h' , the angle pp is about 9°, and hence $C = 85^\circ 30'$. On g' extinction takes place at an angle of about 20° towards the acute angle of the edges p and h' . On h' the extinction is longitudinal, and the elongation is positive in the direction of the longitudinal edges of the prism.

C. H. B.

Witherite from Przibram. By A. HOFMANN (*Ber. k. böhm. Ges.*, 1896, [1895], No. 15, 1—7).—Witherite has recently been found at

one point in the mineral veins of the Przibram district, Bohemia, as greyish- to yellowish-white, pyramidal crystals, which have the usual polysynthetic structure and show curved and uneven faces. Analysis of water-clear material gave

BaO.	CaO.	SrO.	FeO.	CO ₂ .	Insol.	Total.	Sp. gr.
77.54	0.09	trace	0.14	22.16	0.38	100.31	4.25

It is suggested that the witherite has been formed by the action of alkali carbonates, produced by the decomposition of diabase, on barytes, at a temperature higher than 25°; the barytes of the first generation of the district being often corroded and represented by pseudomorphs.

L. J. S.

Chrysocolla in Andesite-tuff. By GYULA PETHÖ (*Földtani Köz-löny*, 1895, 25, 236—237).—Amorphous chrysocolla occurs as crusts and cementing the lapilli in an andesite-tuff, near Guravoj, county of Arad, Hungary; the colour is various shades of green and blue. In the interior are radiated patches of malachite, indicating that the copper was first deposited in the tuff as malachite, which was afterwards altered to chrysocolla. Analysis by A. Kalecsinszky gave SiO₂, 40.20; CuO, 37.37 per cent.

L. J. S.

Variations in the Composition of Apatites. By ADOLPHE CARNOT (*Compt. rend.*, 1896, 122, 1375—1380).—Several specimens of apatite from such widely separated localities as Spain, the Tyrol, Norway, &c., and of very different external appearance, were found to correspond in composition with the well-known formula of Rose. Two specimens from Canadian localities and one from the United States were found to contain a proportion of halogen considerably lower than the normal amount. These specimens, however, contained calcium carbonate, and the carbonic acid therein was found to be equivalent to a quantity of fluorine just sufficient to bring the proportion of halogen up to the normal amount. It would seem, therefore, that calcium carbonate as well as calcium chloride can replace the calcium fluoride. When heated in sealed tubes at 160° with sodium carbonate solution, apatite containing fluorine only was but slightly affected, but apatite containing chlorine also was appreciably altered.

Two transparent, yellowish varieties of apatite from the Tyrol were found to contain a very low proportion of halogen, and practically no calcium carbonate. The cause of this abnormal composition is uncertain, but it is noteworthy that these specimens had no outward crystalline form, although they showed the cleavage, and the optical properties of true apatites.

C. H. B.

An Alpine Nickel-bearing Serpentine. By EMILY A. ASTON and THOMAS GEORGE BONNEY (*Quart. Journ. Geol. Soc.*, 1896, 52, 452—460).—The rock is from the summit of the Riffelhorn, near Zermatt; microscopical examination shows the presence of a colourless, flaky, serpentinous mineral, an augite, magnetite, and awaruite. As shown by the analytical results (I), half the minerals must be anhydrous,

and the amount of iron is not much more than sufficient for the magnetite and awaruite. The amount of nickel present in the awaruite is less than 1 per cent., and the remainder replaces calcium in the pyroxene. Sp. gr. of the rock, 2.71.

	SiO ₂ .	Al ₂ O ₃ .	As ₂ O ₃ .	Fe ₂ O ₃ .	FeO.	CuO.	NiO.	CaO.
I.	41.81	0.68	0.13	5.55	1.42	0.15	4.92	trace
II.	40.26	3.61	—	2.58	2.69	—	—	—

	MgO.	Na ₂ O.	H ₂ O (combined).	Moisture.	Total.
I.	39.86	—	4.90	0.04	99.46
II.	41.35	0.71	9.51	0.17	100.88

Another fragment gave Analysis II (mean of two); here calcium and nickel are both absent, and the figures are nearer to those of an ordinary serpentine, although the alumina is somewhat high. The fulgurites, or lightning-tubes, in these rocks are described in detail.

L. J. S.

[Analysis of Orthoclase from an Odenwald Granite.] By C. CHELIUS (*Jahrb. f. Min.*, 1896, ii, 69—71; from *Notizbl. Ver. f. Erdkunde, Darmstadt*, 1894, [4], 15, 16—39).—Analysis I is of the older granite from Oberwald, near Steinau; the rock contains porphyritic crystals of orthoclase (Analysis II), and in the ground mass there is much plagioclase: hornblende is also present.

	SiO ₂ .	Al ₂ O ₃ .	TiO ₂ .	Fe ₂ O ₃ .	FeO.	CaO.	MgO.
I.	63.86	17.87	0.03	1.24	2.88	3.33	0.99
II.	69.30	14.28	—	0.42	0.28	2.03	0.14

	K ₂ O.	Na ₂ O.	P ₂ O ₅ .	H ₂ O.		SO ₃ .	Total.
				Chem. comb.	Hygroscopic.		
I.	3.56	4.10	0.65	0.84	0.17	—	99.52
II.	9.79	2.11	0.60	0.39	0.07	0.33	99.74

L. J. S.

The Mode of Occurrence of Gold in the Ores [Rhyolite] of the Cripple Creek District. By RICHARD PEARCE (*Proc. Colorado Sci. Soc.*, 1894, 5 [Read January 8, 1894], 8 pp.).—The Cripple Creek ore is a rhyolite, having the joints and cracks lined by psilomelane, with which is associated the gold; pyrites is abundant. In the unaltered rock, gold occurs in combination as telluride (sylvanite), and is associated with fluorite; but in the altered, clayey portions it occurs free, either in a fine state of division or as brittle plates pseudomorphous after sylvanite, the tellurium here being in the oxidised form, as is shown by the fact that it can be readily extracted by hydrochloric acid. The ratio of tellurium to gold in the oxidised ore is higher than that required for sylvanite, indicating that other tellurium minerals (possibly native tellurium) must have been originally present, or that some of the gold has been subsequently removed. It is suggested that the ore has originated by solutions having impregnated the rock with pyrites and sylvanite.

L. J. S.

Further Notes on Cripple Creek Ores. By RICHARD PEARCE (*Proc. Colorado Sci. Soc.*, 1894, 5, [Read April 5, 1894], 7 pp.).—The following analyses, by F. C. Knight, are given of the unoxidised portion (I) and of the oxidised portion (II) of a single specimen of the rhyolite which forms the Cripple Creek ore.

	SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	Fe.	S.	SO ₃ .	MgO.	Te.	TeO.
I.	56.70	19.35	—	4.20	4.75	—	0.37	0.10	—
II.	50.55	19.93	10.57	—	—	2.55	0.12	—	0.78

	Au.	Ag.	MnO ₂ .	H ₂ O.	K ₂ O, Na ₂ O [diff.].
I.	0.041	0.022	—	0.50	[13.967]
II.	0.049	—	0.27	3.05	[12.131]

In the unoxidised portion of the rock, pyrites and sylvanite are present; although the latter is not visible, even with the aid of a lens, its presence is indicated by the relative proportions of gold, silver, and tellurium shown in the analysis. In the oxidised rock, the pyrites is represented by a hydrated basic ferric sulphate near glockerite, the tellurium is present as oxide, and the gold is free, the latter being rarely visible as a soft, brownish deposit. L. J. S.

A suspected New Mineral from Cripple Creek. By F. C. KNIGHT (*Proc. Colorado Sci. Soc.*, 1894, 5, [Read October 1, 1894], 6 pp.).—R. Pearce has previously pointed out the existence of tellurium in an oxidised form in the Cripple Creek ores (see preceding abstracts), and in this paper it is shown to be present as an *iron tellurite*. The specimen examined consists of a crystalline telluride intimately associated with a light brown, brittle, amorphous matrix. Analysis of the whole gave the following results.

Sol. in HCl.					
H ₂ O.	Fe ₂ O ₃ .	TeO ₂ .	SeO ₂ .	Ag.	
0.45	8.12	17.81	0.45	0.22	

Insol. in HCl.					
SiO ₂ .	Au.	Ag.	Te.	Se.	Total.
38.25	18.41	1.20	14.72	0.32	99.95

From the portion insoluble in hydrochloric acid, the telluride was dissolved by nitric acid, and the free gold by aqua regia. The tellurium is present as tellurous, and not as telluric, oxide, as is shown by the fact that no chlorine was evolved, and no gold dissolved, when the material was treated with hydrochloric acid. Eliminating silver (which is present owing to the solubility of silver chloride in tellurium tetrachloride) and calculating to 100, the portion soluble in hydrochloric acid gave the results under I; with another specimen, the results under II were obtained.

	Fe ₂ O ₃ .	TeO ₂ + SeO ₂ .	H ₂ O.	Total.
I.	30.27	68.05	1.68	100.00
II.	35.44	62.79	1.77	100.00

The first of these corresponds with the formula $2(\text{Fe}_2\text{O}_3, 2\text{TeO}_2) + \text{H}_2\text{O}$.

The crystalline telluride when separated from the matrix gave, on analysis, the following results, showing its identity with calaverite (compare this vol., ii, 31).

Au.	Te.	Ag.	Total.
40.14	56.22	3.63	100.00

L. J. S.

Analyses of Spherulites and Matrix of Rocks. By HUGH H. F. HYNDMAN and THOMAS GEORGE BONNEY (*Geol. Mag.*, 1896, 3, 365—371).—Analyses are given of the sea-green matrix (I) and of the reddish spherulites (II) of a pyromeride (rhyolite) from Boulay Bay, Jersey. Under the microscope, the matrix shows a mosaic of quartz and felspar, with plumes and granules of a chloritic mineral and ferrite; the spherulites are not unfrequently traversed by veins of chalcedonic quartz.

	SiO_2 .	Bi_2O_3 , &c.	Al_2O_3 .	Fe_2O_3 .	FeO .	CuO , &c.	NiO .	CaO .
I.	78.40	0.58	8.81	—	4.02	trace	0.29	0.57
II.	73.23	0.51	11.45	4.50	—	0.30	trace	0.38

	MgO .	K_2O .	Na_2O .	H_2O .	Total.
I.	0.20	2.62	3.06	1.53	100.08
II.	0.02	2.77	5.14	0.81	99.11

The matrix therefore contains more quartz and more orthoclase, relatively to albite, than the spherulites; analyses of the matrix and spherulites of an artificial glass, however, show these relations reversed.

L. J. S.

The Costilla Meteorite. By RICHARD C. HILLS (*Proc. Colorado Sci. Soc.*, 1895, 5, [Read January 7, 1895], 2 pp.).—This meteorite, which weighs about 78 lbs., was found in August, 1881, on the north slope of Costilla Peak, about six miles south of the boundary line between Colorado and New Mexico. The etched surface shows bands of kamacite and tænite parallel to the octahedral cleavage. A little troilite, schreibersite, and a substance like graphite are present. An analysis by L. G. Eakins gave

Fe.	Ni.	Co.	P.	S.	Total.
91.65	7.71	0.44	0.10	0.26	100.16

L. J. S.

Meteorite of Lesves. By ALPHONSE F. RENARD (*Bull. Acad. Belg.*, 1896, [3], 31, 654—663).—A meteorite weighing nearly 2 kilos. fell at Lesves in Belgium on April 13th, 1896, burying itself 40 cm. in the ground. Analysis by Stöber gave

SiO_2 .	Al_2O_3 .	Cr_2O_3 .	FeO .	CaO .	MgO .	K_2O .
39.46	3.33	1.02	15.82	1.54	22.75	0.09

Na_2O .	Fe.	Ni.	Co.	S.	Total.	Sp. gr.
1.05	12.36	1.37	0.11	2.25	101.15	3.575

The mineralogical composition is given as

Olivine ($\text{Fe}_2\text{SiO}_4 + 2\frac{1}{2}\text{Mg}_2\text{SiO}_4$).	Bronzite ($\text{FeSiO}_3 + 3\text{MgSiO}_3$).	Nickel- and cobalt-iron.	Troilite. (FeS).	Chromite.
45.88	22.33	9.91	6.18	1.51

Maskelynite and a monosymmetric pyroxene are also probably present.

The structure is chondritic, and both the crystals and the chondrules of olivine and bronzite contain glassy and other enclosures. Under the microscope, the olivine shows undulose extinction and a fragmentary structure similar to mortar-structure; it is, therefore, considered that the paste of the meteorite is a product of cataclastic action. In the crust three zones can be distinguished. L. J. S.

Acid Spring near Rome (Ponte Molle). By G. FELICIANI (*Gazzetta*, 1896, **26**, i, 281—289).—The author has examined the water from an acid spring situated several kilometres from the Porta del Popola, Rome, and at the right of the Via Flaminia; the water is reputed to have a therapeutic value, and was analysed by Morichini in 1820, and by Commaille and Lambert in 1859. The middle one of the three sources enjoys the greatest reputation, and was, therefore, most fully examined.

In January, 1895, the water issued at 14.6° , the atmospheric temperature being 10° , and had the sp. gr. at $14.6^\circ/0^\circ$ of 1.00216. One litre at 0° and 760 mm. contained 356.30 c.c. of free carbonic anhydride, 2.10 c.c. of oxygen, 23.40 c.c. of nitrogen, and the following quantities of various salts in grams.

NaCl.	KCl.	LiCl.	MgCl_2 .	KNO_3 .	$\text{Na}_2\text{B}_4\text{O}_7$.
0.2669	0.1989	0.0115	0.1546	0.0476	0.0190
	NaHCO_3 .	$\text{CaH}_2\text{C}_2\text{O}_6$.	CaSO_4 .	SiO_2 .	
	0.6454	0.8411	0.1463	0.0310	

The water also contains traces of iron, magnesium, aluminium, and iodine.

This spring thus affords the best natural lithia water to be found in Italy. W. J. P.

Water from the Chalybeate Spring of Óvári. By SIGISMUND NEUMANN (*Földtani Közlöny*, 1895, **25**, 268; from *Math és term. tud. Értesítő*, 1892, **10**, 137—138).—Water from a chalybeate spring near Óvári (near Szathmár, Hungary), contained in parts per 1000: CaSO_4 , 0.10431; $\text{Ca}(\text{HCO}_3)_2$, 0.45935; $\text{Fe}(\text{HCO}_3)_2$, 0.14098; $\text{Mn}(\text{HCO}_3)_2$, 0.00239; $\text{Mg}(\text{HCO}_3)_2$, 0.22059; NaHCO_3 , 0.18014; NaCl , 0.04973; KCl , 0.01343; lithium, trace; SiO_2 , 0.03170; humic acids, 0.01660; total solids, 1.21922; free CO_2 , 0.14216.

L. J. S.

Water of the Kaw River and its Tributaries. By EDGAR H. S. BAILEY and EDWARD C. FRANKLIN (*Kansas Univ. Quart.*, 1894, **3**, 91—102).—Analyses are given of the water taken from the Kaw or Kansas River at different points, and also of the waters of its tributaries.

The waters of the tributaries show considerable differences amongst themselves; for example, the Saline River contains 232·30 parts of total solids in 100,000, whilst the Delaware River contains only 39·56 parts; the Kaw River contains 77 parts of total solids in 100,000. The organic matter in these waters is relatively high, and has been derived from the rich prairie soils.

L. J. S.

Physiological Chemistry.

Importance of Digested Crude Fibre as Food. By P. HOLDEFLEISS (*Bied. Centr.*, 1896, **25**, 372—379; from *Ber. phys. Lab. landw. Inst. Univ. Halle*, Heft 12, 52).—The results of direct experiments showed that crude fibre is digested in the rumen, and especially in the cæcum, but not in the abomasum. The crude fibre is partly dissolved by fermentation, and is partly converted into more readily soluble intermediate products, resembling amyloid.

In order to ascertain the food value of digested crude fibre, experiments were made in which a sheep was fed, first with hay alone, next with half the amount of hay together with earth-nut cake, potato starch, sugar, and salt; in the third period, crude fibre was substituted for starch, whilst in the fourth period, the sheep had the same food as before, except starch and crude fibre. A control experiment was made with a second sheep. From the amounts of food constituents actually consumed, and from the amounts and composition of the excrement, it is concluded that, as compared with that of nitrogen-free extract, the food value of crude fibre is, on the average, as 80:100.
N. H. J. M.

Fermentative Processes in the Organs. By CESARE BIONDI (*Virchow's Archiv*, 1896, **144**, 373—400).—E. Salkowski has described a phenomenon which occurs in the organs after death, and which is not putrefaction. He believes it to be due to the action of an enzyme, and terms it "autodigestion." The most marked action is the formation of amido-acids and substances of the xanthine group. Neumeister considers that the action is simply due to trypsin.

The present research was carried out with calves' livers, and putrefaction was prevented by chloroform water, or sodium fluoride; the former reagent appears to be the most efficacious for the purpose. Salkowski's observations are confirmed. The enzyme, however, is not trypsin, for the following principal reasons: (1) in autodigestion, xanthine-like substances are formed; in tryptic digestion, these are present in a "latent" condition. (2) Autodigestion is not inhibited by an acid medium. (3) Tryptophan, the substance which reacts with bromine water, is a product of tryptic, but not of auto-digestion.

W. D. H.

Theory of Lymph-Formation. By WILHELM COHNSTEIN (*Pflüger's Archiv*, 1896, **63**, 587—612).—This paper is largely

polemical, criticisms being directed chiefly against Mendel (this vol., ii, 315). The author still holds that diffusion and filtration will explain lymph-formation: and although he admits that physical and chemical changes in the protoplasm of the endothelial cells will influence the formation of lymph, he still regards the secretion theory as unproved and unnecessary.

W. D. H.

Formation of Sugar by the Liver. By MAX MOSSE (*Pflüger's Archiv*, 1896, **63**, 613—621).—Seegen found, in opposition to Pavy, that the blood of the hepatic vein is much richer in sugar than that of the portal. Cavazzani (*Pflüger's Archiv*, **57**, 181; *Centralbl. f. Physiol.*, **8**, No. 2) has shown that this might be due to stimulation of the sympathetic nerves, causing an increased decomposition of the hepatic glycogen. Other factors which tend to vitiate results are the influence of anæsthetics, the production of muscular struggling if no anæsthetics are given, and faulty methods of estimating sugar.

Accordingly in the present research the blood from the hepatic vein was collected by catheterisation through the jugular vein; the abdominal cavity was not opened at all, and arterial blood collected from the crural artery was used as the blood with which to compare the hepatic blood; the animals (dogs and sheep) had fasted for 24 hours before the operation; during the operation they were lightly morphinised.

In each experiment two portions of each kind of blood were collected: an interval of 10 minutes occurred between the collection of the samples; the second sample always showed an increased percentage of sugar. Coagulation of the blood was prevented by ammonium oxalate, proteid was removed by the addition of metaphosphoric acid, and the sugar was estimated by Allihn's method. The mean of seven experiments gives:

Arterial blood contains 0.093 gram of sugar per 100 c.c.

Hepatic venous blood contains 0.107, or a plus of 0.014 per cent.; this figure is much smaller than Seegen's, but is, nevertheless, in favour of the glycogenic function of the liver, as taught by Bernard. The question as to whether sugar is the principal, or only, source of energy in the organism is not discussed.

W. D. H.

Paralytic Intestinal Juice. By LAFAYETTE B. MENDEL (*Pflüger's Archiv*, 1896, **63**, 425—439).—The so-called paralytic intestinal juice is the secretion that occurs in the intestine after section of its nerves. The present experiments show that it is, nevertheless, a true secretion, and not, as some assume, a transudation from the blood. Its composition, especially as regards its alkalinity and percentage of chlorine, is similar to that of the normal juice as obtained by a fistula. Its small percentage of proteid is against the transudation theory. Its action on food-stuffs is like that of the normal juice; histological examination of the mucous membrane shows no deviation from the normal.

W. D. H.

Alterations in the Blood in Anæmia. By SOPHIE VON MORACZEWSKA (*Virchow's Archiv*, 1896, **144**, 127—158).—In pernicious anæmia, there is a great diminution of the alkalinity of the blood; this fluid has a high specific gravity, a small number of corpuscles—the red corpuscles are rich in pigment—and the blood has its total nitrogen increased. In chlorosis, the blood has a low alkalinity and a high specific gravity; the majority of red corpuscles are deficient in hæmoglobin.

In carcinoma, the blood has a high alkalinity, and a low specific gravity; the total dry residue is small, and the majority of red corpuscles are but feebly pigmented.

W. D. H.

Excretion of Ammonia in Disease. By THEODOR RUMPF (*Virchow's Archiv*, 1896, **144**, 563—568).—Polemical. The author maintains the correctness of his views against those of Hallervorden (compare this vol., ii, 379).

W. D. H.

Action of the Kidney in the Light of the Theory of Osmotic Pressure. By GUSTAV TAMMANN (*Zeit. physikal. Chem.*, 1896, **20**, 180—197).—The osmotic pressures of the various substances which are dissolved in the blood were estimated, and the author then considers the probable filtration action in the glomeruli. The view that in the glomerulus water alone is filtered off must be abandoned, since this would necessitate a blood pressure of over 7·7 atmos., whilst the actual difference of pressure between the blood in the looped veins and the liquid in the glomerulus capsule is probably only about 20 mm. The author considers it, therefore, most probable that all the soluble salts, &c., of the blood are filtered off, with the exception of albumin. The glomerulus filtrate is not, however, urine, and for its conversion requires a concentration of many salts, and especially of urea. This cannot be due to absorption of water by the blood, but how, and in what portions of the tubules, the changes take place, the author has not determined.

L. M. J.

Chemistry of Vegetable Physiology and Agriculture.

Cell-wall of Cotyledons of *Lupinus luteus* and *Lupinus angustifolius*. By ERNST SCHULZE (*Zeits. Physiol. Chem.*, 1896, 21, 392—411).—The conclusions of Elfert (*Bibliotheca botanica*, 1894), Nadelmann (*Ber. d. Bot. Gesel.*, 1889, 248), and Tschirch (*Pflanzen-anatomie*, 1, 453) are not in accordance with the observations of E. Steiger and the author (Abstr., 1887, 440; 1889, 643, &c.), who have shown that the cell-wall of the cotyledons of *Lupinus luteus* and *L. angustifolius* contains a considerable proportion of a substance whose properties are quite distinct from those of ordinary cellulose, and to which they allude as paragalactan. Unlike cellulose, it dissolves readily in 1 per cent. hydrochloric or sulphuric acid, and, on

hydrolysis, yields galactose and a pentose (probably arabinose), and no glucose; further, when oxidised by nitric acid, it gives mucic acid. These facts afford a basis for its approximate quantitative determination.

A definite number of shelled seeds of *L. luteus* or *L. angustifolius* were weighed, powdered, and extracted with water, dilute soda, alcohol, and ether, and the residual, insoluble, non-nitrogenous "paragalactan residue" dried and weighed; the latter was then hydrolysed by dilute sulphuric acid, and the glucose contained in aliquot portions of the solution was determined, a second portion being freed from sulphuric acid by means of barium carbonate, filtered, and evaporated, oxidised with nitric acid, and the mucic acid thus formed, collected and weighed. The cotyledons of embryos, of two or three weeks' growth, were then treated in a similar manner, and the results compared.

In the case of *L. angustifolius*, it was found that whilst the cotyledons of two-week-old seedlings yielded one-tenth of the quantity of glucose and one-twelfth of the amount of mucic acid afforded by the corresponding number of seeds, the cotyledons of three-week-old plants showed no further reduction in the amount of mucic acid obtainable, although the yield of glucose had considerably diminished. Estimations of the total insoluble non-nitrogenous matter showed that three-week-old cotyledons contained only about one-fourth of the amount present in the corresponding number of seeds. Similar results were obtained in the case of *L. luteus*.

From the above data it is clear that the portion of the "paragalactan residue" which gives mucic acid, diminished much more rapidly than that affording glucose, and that the diminution in the former is at an end in two weeks' time. This behaviour is in accordance with the belief, already expressed by the author, that the paragalactan is not a simple substance, but is made up of a galactan and an araban, the former being more rapidly utilised than the latter. The results afford conclusive evidence against the views of Elfert, Nadelmann, and Tschirch.

The author has compared the amounts of ordinary cellulose in the seed of *L. angustifolius*, and in the cotyledons after $2\frac{1}{2}$ weeks' growth, and has found them approximately equal. It is obvious, therefore, that the true cellulose is not absorbed in the initial stages of germination.

A. L.

Decomposition and Assimilation of the Nitrogen Compounds of Stable Manure. By STEF. JENTYS (*Bied. Centr.*, 1896, 25, 419; from *Bull. Acad. Sciences Cracovie*, 1893, 345; compare *Abstr.*, 1894, ii, 110).—In fæces, there may be a rather considerable loss of nitrogen when decomposing under conditions of abundant aeration, without evolution of free nitrogen. Elimination of free nitrogen is independent of nitrification, and does not take place when solid excrement decomposes in absence of air. Loss of ammonia from decomposing fæces is very slight in presence of oxygen, and increased temperature and the presence of lime are then without effect; in absence of oxygen, there is abundant production of ammonia. In presence of urine, there is no increased production of

ammonia from fæces; and the urine-ammonia is partly fixed by the products of the decomposing fæces, a portion of the ammonia so fixed being converted by microbes into stable compounds. Fresh horse dung supplies very little nitrogen to plants when buried in well aerated soil; but it remains to be seen how much the availability of the nitrogen of fæces can be increased by excluding oxygen. The assimilability of the nitrogen of dung which is kept in heaps is considerably diminished, as the available urine-nitrogen becomes converted into forms which are decomposed with difficulty, whilst the nitrogen of the fæces does not become more soluble. N. H. J. M.

Methods of determining the Availability of Organic Nitrogen in Fertilizers. By SAMUEL W. JOHNSON and EDWARD H. JENKINS (*Ann. Rep. Conn. Agric. Exper. Stat.*, 1894, No. 18, 73—112; compare *ibid.*, 1885, 115; 1886, 80; 1893, 218).—A number of pot experiments were made in which maize was grown in artificial soil (anthracite ashes and peat), supplied with the necessary minerals and with different amounts of nitrogen in the form of sodium nitrate, dried blood, fish, tankage, ground horn, cotton seed and linseed meals, castor pomace, and raw, roasted, and steamed leather. Soil extract was added to several pots with the view of supplying nitrifying organisms. The amount of produce and of nitrogen contained in it were determined. With regard to the effect of inoculation, the results indicate that, whether nitrification is essential or not to the utilisation of organic nitrogen, artificial inoculation was unnecessary under the conditions of the experiments. Comparing the availability of the nitrogen of the different manures used, and taking sodium nitrate as 100, the following numbers show the relative availability of nitrogen in the substances named: castor pomace (B) = 85; linseed meal = 80; blood = 77; cotton seed meal = 76; castor pomace (A) = 74; horn and hoof = 72; dry fish = 70; and tankage = 68 per cent. Finely powdered, raw leather was absolutely inert, and steamed and roasted leather was almost worthless. The nitrogen of leather which had been heated with sulphuric acid seemed to be as available as that of dried fish.

The solubility of the nitrogen of the same substances in pepsin solution was next determined. When the results are multiplied by 0.826 (which makes the figure obtained with dried blood the same as the figure obtained for the same substance in the vegetation experiments), the two sets of results agree fairly in most cases, so that the solubility of the nitrogen of these substances in pepsin solution is a fairly good indication of the relative availability of the nitrogen for the maize plant under the conditions of the experiments. With horn and hoof, steamed leather, and dissolved leather, the two sets of results were, however, totally different.

Finally, the amount of nitrogen rendered soluble during putrefaction (two and four weeks) was determined, but the results showed no satisfactory agreement, either with those obtained by the pot experiments or by solubility in pepsin solution. N. H. J. M.

Action of Vegetable Acids on Insoluble Phosphates in presence of Nitrates. By GUSTAV LOGES (*Bied. Centr.*, 1896, 25, 366—

367; from *Verhandl. Ges. Deut. Naturforsch.*, 1896, 84).—When basic slag (2 grams) is treated with 2 per cent. hydrogen potassium oxalate solution (250 c.c.) for 48 hours, 27—47 per cent. of the total phosphoric acid is dissolved. Crude phosphates similarly treated give up 40—98 per cent. of the total phosphates. In presence of potassium nitrate (0.08—0.16 per cent.), the solubility of the phosphoric acid of basic slag is much increased (as much as from 28 to 68 per cent.), whilst with crude phosphates this is not the case. In basic slag, the particles of phosphate are encased in a strongly basic, calcareous substance, which is rendered insoluble by oxalic acid, and so protects the phosphate from the action of the acid. When a nitrate is present, nitric acid is liberated by the oxalic acid, and the calcium oxalate dissolved as nitrate. The same amount of nitric acid is alternately liberated and combined with lime, and the oxalic acid is thus enabled to reach the phosphate. Since in crude phosphates the calcareous covering does not exist, the presence of nitrate is without effect. Nitrate has also no effect when citric and tartaric acids are used as solvents for phosphoric acid. N. H. J. M.

Analytical Chemistry.

A Compensation Method in Gasometry. By CARL VON THAN (*Zeit. physikal. Chem.*, 1896, **20**, 307—320).—The author describes a form of eudiometer in which the corrections for temperature and pressure are eliminated. The principle of the method is the use of a similar tube containing a definite quantity of nitrogen which can be brought to either of four volumes, equal respectively to 1.25, 1.428, 2.0, and 5.0 times the normal volume. Arrangements are described for bringing the two tubes to the desired positions, so that the level of the mercury is the same in both, and corresponds with one of the observation marks in the compensation tube. Experiments are recorded indicating the accuracy of the instrument.

L. M. J.

Volumetric Estimation of Hydrofluoric acid. By KARL F. STAHL (*J. Amer. Chem. Soc.*, 1896, **18**, 415—425).—The strength of the commercial acid, if fairly pure, may be conveniently taken by means of a hydrometer made of platinum, but the following method is preferable.

Total acidity. Two grams of the sample is added to a measured volume of normal soda, allowing the liquid to remain faintly acid; after adding phenolphthalein and warming to 50°, the titration is completed.

Hydrofluosilicic acid. Two grams is diluted in a platinum dish with 5 c.c. of water, and partially neutralised with potassium carbonate, employing 0.05 gram for each c.c. of normal soda used in taking the total acidity; alcohol is now slowly added until the mixture

contains 50 per cent. of it, and the whole is left for some time before the precipitate of potassium silicofluoride is collected; after washing it with 50 per cent. alcohol, the precipitate is put into a platinum dish, mixed with 25 c.c. of water, and titrated with normal soda. 1 mol. of potassium silicofluoride requires for neutralisation 4 mols. of sodium hydroxide; every 6 mols. of the latter correspond with 1 mol. of hydrofluosilicic acid.

Sulphuric acid. Four grams of the sample is evaporated in a platinum dish on the water bath until no more acid fumes are given off. The residue is then diluted with water and titrated with normal soda.

L. DE K.

Estimation of Sulphur in Pyrites. By THOMAS S. GLADDING (*J. Amer. Chem. Soc.*, 1896, 18, 446—449).—A controversy with Lunge (*Abstr.*, 1895, ii, 411). The author again points out that if barium chloride is added all at once to a solution of a sulphate, the precipitated barium sulphate is strongly contaminated with the chloride. If, however, the barium solution is added drop by drop to the boiling solution and excess be avoided, the barium sulphate will be practically pure.

L. DE K.

Detection of Nitrites by means of Cuprous Salts. By PAUL SARATIER (*Compt. rend.*, 1896, 122, 1417—1419).—When a small quantity of a nitrite is dissolved in concentrated sulphuric acid, and a few particles of cuprous oxide are added, a very intense violet-purple coloration is produced. All cuprous salts produce the same result, although in the case of the dry chloride the coloured product forms slowly. With cuprous iodide, the iodine is liberated, but can be removed by means of chloroform, in which the purple compound is insoluble. Finely divided reduced copper dissolves in the sulphuric acid solution of the nitrite, giving the violet coloration; cupric salts show no similar reaction, nor do salts of many other metals.

The violet-purple solution loses its colour slowly, even in sealed tubes out of contact with air; the change is accelerated by heat, and takes place immediately if the liquid is agitated with air or if oxidising agents are added. Water, or sulphuric acid mixed with one-fifth its volume of water, also destroys the violet compound.

In order to apply this reaction to the detection of nitrites, a very small drop of the liquid is mixed on a porcelain plate with a drop of concentrated sulphuric acid, and a few particles of cuprous oxide are added. It is not so sensitive as the metaphenylenediamine reaction.

C. H. B.

A Modified Ammonium Molybdate Solution. By A. L. WINTON (*J. Amer. Chem. Soc.*, 1896, 18, 444—445).—One thousand grams of molybdic acid is dissolved in 4160 c.c. of a mixture of 1 part of ammonia (sp. gr. 0.90) and 2 parts of water. 5300 grams of ammonium nitrate is dissolved in a mixture of 6250 c.c. of nitric acid (sp. gr. 1.4) and 3090 c.c. of water, and the molybdate solution is added to it slowly with constant stirring. After a few days, the clear liquid is poured off for use.

This solution differs from Fresenius's solution in that it contains in 50 c.c. an extra 15 grams of ammonium nitrate. The author

claims that the new solution causes a more rapid and complete formation of the yellow phosphoric acid precipitate. L. DE K.

A Simple Method for determining the Neutrality of the Ammonium Citrate Solution used in the Analysis of Fertilisers.

By NATHANIEL W. LORD (*J. Amer. Chem. Soc.*, 1896, 18, 456—457).—Pure litmus solution is added to 200 c.c. of distilled water until this is faintly coloured. Half of this is then diluted with its own volume of water; three clear 50 c.c. Nessler tubes are taken, and two are filled with the diluted liquid, and the third to the same depth with the stronger solution. To one of the two first, a drop of dilute sulphuric acid is added, and to the other, a drop of ammonia. These tubes are set one in front of the other, so that the light passes through both, thus giving a strictly neutral purple colour. To the liquid in the third tube is now added 5 c.c. of the citrate solution to be tested, and the colour is then compared with the colour shown by the doubled tubes. The slightest acidity or alkalinity is then at once noticed, and the amount of either acid or alkali necessary to make it neutral may be rapidly ascertained. L. DE K.

Separation of the Insoluble Phosphoric acid derived from Bone Phosphate from that derived from Mineral Phosphate.

By A. P. BRYANT (*J. Amer. Chem. Soc.*, 1896, 18, 491—498).—As the value of the phosphate insoluble in ammonium citrate is not the same in these two classes of phosphates, a method for separating and estimating them is desirable. The following separating solution is required:—75 grams of potassium iodide and 100 grams of mercuric iodide is dissolved in 350 c.c. of water and evaporated to a sp. gr. of 2.26. The liquid should be kept in a wash bottle.

The special apparatus required consists (1) of a separating tube, made of two tubes about 13 mm. internal diameter, one being 70 mm. in length, closed at one end, the other 200 mm. long, and open at both ends, and connected by a short piece of stout rubber tubing, sufficiently long to allow of the lower closed tube or "bucket" being separated by a screw pinch-cock from the upper portion. (2) An extraction tube, 25 mm. internal diameter, slightly contracted at one end, which has a rim, over which filter paper and cheese cloth can be tied.

In carrying out the separation, 2 grams of the sample is transferred to the extraction tube, and washed with 100—225 c.c. of hot water. After thoroughly drying, it is most carefully removed and transferred to the separating tube; 15—20 c.c. of the separating solution is then poured into the tube, thoroughly shaken, and the sides washed down with a jet of the solution. After five minutes, the lower part of the tube is tapped smartly with the finger to release any light portion carried down with the heavy, and the matter on the top is stirred up with a jet of solution. After the solution has cleared, the rubber tube is clamped, and a beaker is placed under the "bucket," which is then carefully removed, the fingers being protected by india-rubber finger tips. The solution in it containing the mineral phosphate is filtered into the supply flask, the first washings being again evapo-

rated to a sp. gr. of 2.26, and the insoluble phosphoric acid is treated in the usual way. The light portion from the upper tube is treated in a similar manner. If desired, the heavy and light portions can be treated as for total phosphoric acid, thus determining all the phosphoric acid derived from inorganic and organic sources, except that soluble in water.

L. DE K.

Rapid Estimation of Carbonic Anhydride in the Atmosphere, &c. By HENRIET (*Compt. rend.*, 1896, 123, 125—127).—The method described makes use of the fact that a solution of normal potassium carbonate, coloured by a drop of phenolphthalein, becomes colourless on the addition of sulphuric acid, the instant the first trace of carbonic acid is set free after the neutral carbonate has become converted into the bicarbonate. The carbonic anhydride in a given volume of air is absorbed by potash and the liquid titrated, an equal volume of the original potash solution is also titrated, and the difference between the titrations multiplied by two gives the amount of carbonic anhydride absorbed. It is obvious that the amount of carbonate in the original potash need not be taken into account.

The apparatus suggested consists of a flask of about 6 litres capacity, fitted with a caoutchouc cork, through which pass a dropping funnel, and a tube bent at right angles and provided with a cock. A given volume of potash, coloured with phenolphthalein, and covered with a layer of ether to prevent the absorption of carbonic anhydride from the air, is run into the flask, containing the sample of air, by means of the dropping funnel; the latter is then thoroughly washed out with distilled water, previously boiled to remove carbonic anhydride, and the flask is agitated at intervals during one hour. The potash solution in the flask is then titrated.

J. J. S.

Estimation of Potassium. By CHARLES FABRE (*Compt. rend.*, 1896, 122, 1331—1333).—Potassium platinochloride, precipitated and washed in the usual way, is dissolved in hot water, and reduced to the metallic state by adding magnesium powder previously washed with alcohol and water. The chlorine in the liquid is estimated by means of silver nitrate solution, using potassium chromate as the indicator. A small quantity of insoluble magnesium oxychloride often forms during the reduction, and it is therefore advisable to add a few drops of sulphuric acid; after the reduction is complete, filter, neutralise with calcium carbonate, and then titrate.

C. H. B.

The End Point in Gay-Lussac's Method of Silver Titration. By C. HOITSEMA (*Zeit. physikal. Chem.*, 1896, 20, 272—282).—In the titration of silver by Gay-Lussac's method, the end point of the reaction is, according to Mulder, the "neutral point" at which both silver nitrate and sodium chloride produce a precipitate in the clear, supernatant liquid. The existence of this neutral point is explained by the author by the solubility of silver chloride. As the compound is also present in the solid state, the product of the concentrations of its ions must remain constant, and hence the addition of either silver or chlorine ions must cause a precipitation of the salt. From Stas's

experiments on the sensitiveness of the reaction, the author calculates that in 100 c.c. 23×10^{-5} millimol is the least quantity capable of giving an observable precipitate, *i.e.*, about 1 part in 3,000,000, and from other experiments similar values are obtained. A similar neutral point is not observed in titrating with a bromide or iodide, because the solubility is less than the amount necessary to produce the apparent precipitate. L. M. J.

Solubility of Barium Sulphate. By FRIEDRICH W. KÜSTER (*Zeit. anorg. Chem.*, 1896, **12**, 261—271).—The author criticises the work of Fresenius and Hintz on the solubility of barium sulphate in water. These chemists found the solubility to be 1 in 100,000 parts of water. If, however, a solution of barium sulphate of this strength is prepared in the manner described by Fresenius and Hintz, and is then treated with pure barium sulphate, the electric resistance of the solution gradually decreases from 0.000085 to 0.000020, and then remains constant, and since the electric resistance is proportional to the concentration, it follows that this saturated solution of barium sulphate contains 1 in 425,000 parts. This number agrees closely with that obtained by Kohlrausch, Rose, and Holleman.

The author also criticises the work of Fresenius and Hintz on the solubility of barium sulphate in various salts and acids, and comes to the conclusion that the results obtained by them are only qualitative, and that the solubility varies in accordance with the action of mass, and the reciprocal influence of electrolytes on solution.

E. C. R.

Volumetric Estimation of Lead. By ANTONIO LONGI and L. BONAVIA (*Gazzetta*, 1896, **26**, i, 327—403).—The authors have carefully examined most of the methods suggested for determining lead volumetrically, in order to ascertain whether any of them possess sufficient accuracy to replace the ordinary gravimetric methods.

Trials were made of Domonte's process (*J. pr. Chem.*, 1846, **38**, 306), which consists in titrating a lead salt, dissolved in excess of potash, with sodium sulphide solution, and of Casamajor's modification of the method (*Abstr.*, 1882, 776); the two methods are not to be recommended owing to the uncertainty of the end reaction.

Hempel's method (*Jahresb.*, 1853, 627) of determining lead by adding oxalic acid, separating the lead oxalate, and determining the oxalic acid either in the precipitate or in the solution by potassium permanganate, gives excellent results if certain precautions are taken. Considerable excess of oxalic acid must be added, and the solutions must be concentrated, lead oxalate being slightly soluble in water, but less so in oxalic acid solutions; the presence of even 0.066 per cent. of nitric acid interferes slightly with the determination of oxalic acid by permanganate. Alcohol should be added to the solution in which the precipitation is performed, and the precipitate should be washed with dilute alcohol, decomposed by sulphuric acid, and the oxalic acid titrated with permanganate.

Schwarz proposed (*Dingl. polyt. J.*, 1863, **169**, 284) to titrate lead solutions, in presence of sodium acetate, with potassium dichromate, determining the end of the titration by mixing drops of the super-

nant liquid with silver nitrate solution. Notwithstanding Schwarz's statement to the contrary, the authors find that the precipitate of lead chromate does not settle with sufficient rapidity for volumetric work; they find also that freshly precipitated lead chromate reacts with silver nitrate giving silver chromate, so that the indication of the end of the titration may be masked. The method gives low results.

The process described by Pellet (this Journal, 1877, i, 227), depending on precipitating the lead with a chromate and determining the excess of the latter volumetrically, is in several respects unsound, and therefore gives bad results. The authors propose the following modification of Pellet's method: Sodium acetate solution is added to the concentrated lead solution, and then standard potassium dichromate is run in until the liquid becomes decidedly yellow; the solution is filtered, and the precipitate washed with the least possible quantity of water. The filtrate is conveniently diluted, and 2 parts of 100 c.c. taken; to each of these is added 5 c.c. of sulphuric acid, and then a standard solution of ferrous ammonium sulphate until the solution is green with no trace of the yellow tint of the chromate. The excess of ferrous salt is then titrated with permanganate, and the quantity of lead in the original solution calculated. The test results are very satisfactory.

Diehl's method (Abstr., 1880, 752), in which the excess of dichromate added to a lead solution is determined by sodium thiosulphate, cannot be depended on; the equation $4K_2Cr_2O_7 + 3Na_2S_2O_3 + 13H_2SO_4 = 3Na_2SO_4 + Cr_2(SO_4)_3 + 4K_2SO_4 + 13H_2O$, which Diehl uses, is incorrect, so that the equivalent values of the thiosulphate must be found by titration against the dichromate.

Roux (Abstr., 1881, 849) has devised a method for determining lead volumetrically, which is widely used; it consists in precipitating the lead by potassium dichromate in presence of sodium acetate, and estimating the excess of dichromate by standard ferrous ammonium sulphate, using potassium ferricyanide as an indicator. The authors failed to get trustworthy results with this method as it stands, but the results are much improved by acidifying the filtrate from the lead chromate with sulphuric acid and running it into a definite quantity of standard ferrous salt, until the latter gives no reaction with ferricyanide, or reducing the chromic acid by adding standard ferrous solution and estimating the excess of the latter by titration with standard dichromate; very dilute potassium ferricyanide strongly acidified with sulphuric acid should be used as an indicator. Very satisfactory results are obtained by this modified process in dilute lead nitrate solutions, which are neutral or contain free acetic acid; the solution, however, should not contain acetates.

The method of titrating chromates by adding potassium iodide and hydrochloric acid and estimating the liberated iodine with thiosulphate (Mohr, *Zeits. anal. Chem.*, 1863, 2, 247) can be applied to the volumetric determination of lead; the titration with thiosulphate can be performed immediately after adding the hydrochloric acid. Sodium acetate is added to lead nitrate solution, and then excess of dichromate is run in; the lead chromate is filtered off,

washed, and the filtrate made up to a standard volume, in which the excess of dichromate is determined by potassium iodide and thiosulphate. The chromic acid in the precipitate may also be determined by dissolving it in caustic potash, diluting to a known volume, adding potassium iodide, then hydrochloric acid, and estimating the liberated iodine with thiosulphate; the results are excellent, but N/100 potassium dichromate should be used, or the solution must be so dilute that the green colour of the chromic salt does not interfere with the end reaction (compare Crismer, *Abstr.*, 1884, 1078).

The volumetric estimation of lead by titration with standard potassium ferrocyanide has been studied by Graeger (*Zeits. anal. Chem.*, 1865, 4, 438) and Yvon (*Abstr.*, 1889, 549). The authors add to a solution of lead nitrate not more than 3 per cent. of potassium nitrate, and then run in an excess of standard potassium ferrocyanide; the precipitate is filtered and washed with 3 per cent. potassium nitrate solution until the filtrate gives no reaction with ferric chloride. The ferrocyanide in the filtrate is determined by permanganate after acidification with sulphuric acid; the precipitated lead ferrocyanide, Pb_2FeCy_6 , also may be dissolved in sulphuric acid and titrated with permanganate. Care must be taken to avoid atmospheric oxidation of the ferrocyanic solution, but otherwise the method is a practicable and accurate one.

The authors have made many trials of Haswell's method (*Dingl. polyt. J.*, 1881, 241, 393), modifying it in various ways, but do not find it suitable for the volumetric estimation of lead. W. J. P.

Electrolytic Estimation of Iron, Nickel, and Zinc. By HUDSON H. NICHOLSON and S. AVERY (*J. Amer. Chem. Soc.*, 1896, 18, 654—659).—Iron when deposited from an alkaline tartrate solution generally contains a trace of carbon, which compensates somewhat for the incomplete precipitation. When citric acid is used, the amount of carbon is still larger. Formates or oxalates do not deposit any carbon. The author has found that, when using Classen's well-known ammonium oxalate process, the electrolytic precipitation of the metal is much facilitated by the addition to the solution (150 c.c.) of a saturated solution of borax (5 c.c.). Nickel has no tendency to carry down with it any carbon, and its electrolytic estimation is, on the whole, satisfactory. As regards zinc, the authors got very satisfactory results in the presence of formic acid partially neutralised with sodium carbonate; a compact, well adhering, evenly distributed, and metallic looking deposit was obtained.

L. DE K.

Sources of Error in Volhard's and similar Methods of Estimating Manganese in Steel. By GEORGE AUCHY (*J. Amer. Chem. Soc.*, 1896, 18, 498—511).—The author has made a large number of experiments on this process, and comes to the conclusion that the following are sources of error in Volhard's process.

(1) The incomplete neutralisation by zinc oxide, usually giving too high results. (2) The too sudden addition of the necessary excess of zinc, frequently giving results which are too low. (3) The titra-

tion in nitric acid solution, giving results about 0.01—0.02 per cent. too high. (4) Neutralisation by zinc oxide in hot solution, giving results which are too high.

In every case a blank experiment should be made, to ascertain the amount of manganese contained in the zinc oxide or other reagents.

The author prefers Stone's modification of Volhard's method as being easier and more rapid than the original. L. DE K.

Estimation of Lactose in Milk by double Dilution and Polarisation. By HARVEY W. WILEY and ERWIN E. EWELL (*J. Amer. Chem. Soc.*, 1896, **18**, 428—433).—The authors have endeavoured to determine the exact correction to be made for the volume occupied by the coagulum when clarifying the milk for polariscopic purposes.

Two portions of milk, of 65.82 grams each, are treated with 10 c.c. of solution of mercuric nitrate, prepared by dissolving the metal in twice its weight of nitric acid (sp. gr. 1.42), and diluting with 5 vols. of water. The one mixture is diluted to 100 c.c., the other to 200 c.c., and, after filtering, their respective rotations a and b are observed at 20° . The corrected rotation a' corresponding with a , allowance being made for the volume of the coagulum, is calculated from the equation $a' = \frac{ab}{a - b}$. The volume x of the precipitate is calculated from the equation $x = \frac{100(a - 2b)}{a - b}$.

L. DE K.

Toxicological Examination for Mercuric Cyanide. By DIOSCORIDES VITALI (*L'Orosi*, 1896, **19**, 80—87).—Mercuric cyanide would not be detected by the ordinary toxicological methods for detecting cyanides, because it is not decomposed by the feeble acids, such as tartaric acid, used to liberate the hydrogen cyanide.

The author proposes to use a method of detecting mercuric cyanide based on the fact that this salt is converted by magnesium into magnesium cyanide, which, when heated in aqueous solution, is wholly decomposed into magnesia and hydrogen cyanide. The material to be investigated is put into a retort, mixed with the liquid which accompanies it or, in default of this, with water, and magnesium dust is added; the retort is then heated on the water bath and the vapours caused to pass through very dilute caustic soda. If it is permissible to evaporate the contents of the retort to dryness, all the hydrogen cyanide can be driven off, but, if this be inadvisable, dilute acetic acid may be added to drive off the last traces of hydrogen cyanide. W. J. P.

Analysis of Wool-grease. By FERDINAND ULZER and HEINRICH SEIDEL (*Zeit. angew. Chem.*, 1896, 349—350).—The authors recommend the following process: 20 grams of potassium hydroxide is dissolved in 20 c.c. of water contained in a hemispherical dish of about 350—500 c.c. capacity. The solution is heated to boiling, and 20 grams of melted wool-grease is introduced with vigorous stirring. After boiling for another minute, the dish is placed on the water bath

until saponification seems complete; to make sure, however, the dish is placed for another two hours inside the water oven. The soap is then dissolved in 250 c.c. of boiling water, restoring from time to time the water lost by evaporation, and when completely dissolved 40 c.c. of hydrochloric acid, slightly diluted, is added. When the fatty mass is perfectly melted, it is, after cooling, removed, and then repeatedly boiled with water until the washings no longer show an acid reaction. After cooling, the fatty cake is removed, dried between blotting paper, and finally dried in the water oven. The total acidity number is then taken by means of Benedikt and Mangold's process. Three samples of Australian wool-grease gave, respectively, the figures 100.2, 102.9, and 101.9. Three South American samples gave the figures 96.4, 96.7, and 96.9.

To form an opinion on the genuineness of wool-grease, the authors also recommend taking the actual acidity number and the Reichert-Meissl number. Its iodine absorption may also be determined.

L. DE K.

A New Test for Asparagine. By L. MOULIN (*J. Pharm.*, 1896, 3, 543).—"Saccharin," warmed with sulphuric acid and a little resorcinol, turns yellowish-green, and if water is now added, and the mixture neutralised with ammonia or aqueous soda, a strongly fluorescent liquid is obtained. The author has found that a similar fluorescence of a fine green tint is produced when asparagine is treated in this way. The same reaction is also given by a crystalline compound, which the author has separated from a cold infusion of liquorice by means of dialysis.

L. DE K.

Test for Cinchona Alkaloids. By JAWOROWSKI (*J. Pharm.*, 1896, 3, 553; from *Pharm. Zeits. Russ.*, 1896, 6).—A mixture is made of equal parts of a 10 per cent. solution of sodium thiosulphate and a 5 per cent. solution of copper sulphate, and at once added drop by drop to 5 c.c. of the liquid to be tested. In presence of quinine, quinidine, cinchonine or cinchonidine, a yellow, amorphous precipitate is formed; if no precipitate is formed after the lapse of a minute, quinine, &c., is absent; the reagent itself giving a precipitate after a time.

The reaction takes place not only in aqueous solutions, but also in solutions made with chloroform, ether, or amylic alcohol.

L. DE K.

Estimation of Caffeine in Tea. By AUGUSTE PETIT and P. TERRAT (*J. Pharm.*, 1896, 3, 529—534).—The authors have found that the use of magnesia or lime is superfluous, and that the alkaloid may be completely extracted from tea by direct treatment with chloroform, provided the tea is moist; dry tea yielding but very little caffeine to chloroform. The following method is recommended. 25 grams of powdered tea is treated with thrice its weight of boiling water and, after 15 minutes, the whole is evaporated on the water bath until the liquid has disappeared, but the residue remains still visibly moist. It is then introduced into a percolator and repeatedly exhausted with

chloroform to extract the caffeine. The chloroform is distilled off, and the residue taken up with boiling water, which, on evaporation, will generally yield a residue sufficiently pure to be at once weighed.

If the alkaloid should be contaminated with chlorophyll, it must be treated with dilute sulphuric acid (1 : 10), filtered, neutralised with ammonia, and evaporated completely to dryness; the residue is then extracted with chloroform, and, after distilling off the latter, the pure caffeine can be weighed.

L. DE K.

Estimation of Nicotine and Ammonia in Tobacco. By VIKTOR VEDRÖDI (*Zeits. anal. Chem.*, 1896, **35**, 309—311).—A continuation of the controversy between the author and Kissling (see this vol., ii, 401). The author states that he used light petroleum and ethylic ether indifferently, having assured himself that the former "gave just as accurate results" as the latter. He reaffirms the fact of soda being carried over when Kissling's own apparatus is employed. The fact that the addition of ammonium chloride did not influence the nicotine titration when working in the manner he proposes (*Abstr.*, 1895, ii, 541) he attributes to the complete volatilisation of the ammonia during the extraction with ether, the ether used being as free from water as possible, and the condenser being cooled with water of ordinary temperature.

With regard to the objection that the amido-compounds in tobacco would yield ammonia when boiled with soda, he considers that his experiments on this subject (*Abstr.*, 1894, 371) show that the decomposition of proteids by soda is too imperfect to influence the estimation of nicotine and ammonia in tobacco. Moreover, in the fermentation which occurs during the manufacture of tobacco from the leaves, most of the amido-compounds and proteids are destroyed. With regard to the errors of calculation imputed to him by Kissling, he ranges his "practical" results against the "theoretical" arguments of the latter.

M. J. S.

Distinction between Magenta and "Acid Magenta." By PAUL CAZENEUVE (*J. Pharm.*, 1896, **3**, 595—597).—A well-known and very delicate reaction for the presence of aldehydes in commercial alcohol is based on the violet colour produced when the sample is mixed with a solution of a rosaniline salt which has been previously decolorised by the addition of sulphurous acid.

The author points out that magenta and "acid magenta" do not behave in the same way. The article consisting of rosaniline hydrochloride gives the coloration, whereas the sulphonated (S) compound does not, a fact which has been overlooked by Lefèvre.

L. DE K.

Examination of Red Wines for Foreign Colouring Matters. By ALBIN BELAR (*Zeits. anal. Chem.*, 1896, **35**, 322—323).—Most of the coal tar dyes give coloured solutions with nitrobenzene, whilst the natural blue and red vegetable colours are insoluble. To make the test, about 5 c.c. of the wine is shaken in a test tube with an equal volume of pure nitrobenzene, first gently, then violently, and if an emulsion

is produced it is caused to separate by warming. Rosaniline, purpurin, and safranin dissolve unchanged; methylene-blue is partially dissolved with an emerald-green coloration; eosin and rosolic acid both leave yellowish insoluble portions. Indigo carmine (sodium indigotin-disulphonate) is quite insoluble. M. J. S.

Quantitative Separation of Proteïds in Beer Wort. By N. C. HENRIK SCHJERNING (*Zeits. anal. Chem.*, 1896, **35**, 285—296).—The extended experience which the author has by this time acquired in the method of wort analysis suggested by him in 1894 (*Abstr.*, 1894, ii, 371; and 1895, ii, 428) has enabled him to systematise and simplify the operations so as to form a process of practical value. Six reagents are now employed, namely, stannous chloride, lead acetate, acetic acid, uranium acetate, ferric acetate, and magnesium sulphate. The stannous chloride is prepared by dissolving 50 grams of tin in hydrochloric acid, evaporating to 130 grams, diluting to 1 litre, and rapidly filtering. It must be kept in small stoppered bottles. The lead acetate solution is approximately a 10 per cent. one, containing 10—12 drops of 45 per cent. acetic acid to the litre. The acetic acid is made by diluting 15 c.c. of the 45 per cent. acid to a litre. The uranium acetate solution is a cold saturated one, obtained by cooling and filtering one prepared at a higher temperature. "Scale" ferric acetate is preserved in the dry state, and dissolved just before use, taking always 0.8 gram to 40 c.c. of the above acetic acid diluted with 100 c.c. of water.

The stannous chloride precipitate, which is regarded as albumin, is obtained by adding 5 c.c. of the reagent to 25 c.c. of wort, allowing the mixture to repose for 4—6 hours at the ordinary temperature, collecting on an 11-cm. extracted filter, washing twice with cold water without suction, and estimating the nitrogen according to Kjeldahl's method. No correction for solubility is needed. Lead acetate precipitates the albumin and denucleïn; about 6 c.c. of the reagent is added to 25 c.c. of wort, the mixture heated to boiling, and the precipitate collected immediately and washed with cold water. In consequence of its solubility, a correction of 0.15 c.c. of N/10 acid must be applied for each 100 c.c. of filtrate + washings. For the ferric acetate precipitation, the reagent prepared as above is heated to boiling and mixed with 20 c.c. of wort. After boiling again, the precipitate is collected and washed with boiling water. No correction for solubility is required. The precipitate contains the albumin, denucleïn, and propeptone. The uranium precipitate contains the above proteïds together with the peptone; 20—25 c.c. of the reagent is added to 25 c.c. of wort, the mixture boiled, and then left to cool until next day in a dark place. The precipitate is washed with cold 1—2 per cent. uranium acetate solution; an addition of 0.1 c.c. of N/10 acid is made for each 100 c.c. of filtrate and washings. In cases where the ferric acetate precipitate is obtained with difficulty, the albumin and propeptone are thrown down by magnesium sulphate; 20 c.c. of the wort, mixed with 5 drops of 45 per cent. acetic acid, is warmed in a water bath to 36°, and 18—20 grams of pulverised crystalline magnesium sulphate is dissolved in it by stirring. It is then left at the ordi-

nary temperature for $\frac{1}{2}$ —1 hour, filtered, and the precipitate washed with a cold saturated solution of magnesium sulphate containing 4—5 grams of 45 per cent. acetic acid to the litre. Zinc sulphate gives identical results (see Bömer, this vol., ii, 83). An experiment made with the dialysed solution of the magnesium sulphate precipitate showed that the presence of saline substances was essential to the precipitation by stannous chloride and ferric acetate, and yielded, moreover, some anomalous results, which up to the present the author has not been able to interpret.

M. J. S.

Estimation of Phosphorcarnic acid. By BALKE and IDE (*Zeits. physiol. Chem.*, 1895, **21**, 380—386).—In estimating phosphorcarnic acid by precipitation as carniferrin (see Abstr., 1895, i, 313) the use of ferric chloride entails the possibility of dissolving some of the precipitate by excess of the reagent; and ferric ammonium alum cannot be employed, as the aqueous solution, when boiled, deposits a small quantity of insoluble nitrogenous matter. The following process is found to yield concordant results.

The dilute meat-extract is heated, to coagulate albumin, and filtered, the phosphates present being then precipitated with calcium chloride and ammonia. The filtrate is neutralised, heated to boiling, and mixed with a 1 per cent. solution of ferric chloride, the latter being carefully delivered from a burette; when a slight excess has been added, the whole is boiled for about two minutes, the addition of ferric chloride being discontinued if the excess be permanent; the liquid is then neutralised with a few drops of ammonia, and finally separated from the precipitate by decantation, the latter process being employed in washing the sediment. The total nitrogen in the dry carniferrin is then estimated and calculated as carnic acid.

A. L.

General and Physical Chemistry.

Optical Rotation of Stereoisomerides. By PAUL WALDEN (*Zeits. physikal. Chem.*, 1896, **20**, 377—383).—As the effect of constitution on the optical rotation of stereoisomeric compounds had not been previously investigated, the author has determined this constant in the case of a number of compounds which are derived from fumaric and maleic acids. The numbers obtained are given in the accompanying table.

Compound.	Specific rotation.	Molecular rotation.	Mol. ref.	Mol. ref. calc.
Amylic maleate	+ 4·62°	11·82°	70·29	69·89
Amylic fumarate	+ 5·93	15·17	70·89	69·89
Amylic chloromaleate . . .	+ 4·03	11·70	75·26	74·83
Amylic chlorofumarate . .	+ 5·78	16·78	75·53	74·83
Amylic bromomaleate . . .	+ 4·58	15·36	81·02	77·76
Amylic bromofumarate . .	+ 5·99	20·07	80·00	77·76
Amylic citraconate	+ 4·14	11·17	75·11	74·49
Amylic mesaconate	+ 5·93	16·01	75·52	74·49
Amylic itaconate	+ 4·97	13·42	74·92	74·49
Maleinoid amylic di- methylsuccinate	+ 3·42	9·79	79·08	79·48
Fumaroid amylic di- methylsuccinate	+ 3·66	10·47	79·40	79·48
Amylic mesotartrate	+ 4·77	13·83	73·54	73·32
Amylic racemate	+ 3·37	9·77	73·26	73·32

The rotation of the itaconate was also observed after the compound had hardened to a glassy mass, probably owing to polymerisation, but the rotation was practically unaltered. It appears from these results, that in these isomerides, the fumaric derivatives have, on an average, a molecular rotation 4·5° greater than that of the maleic derivatives. The molecular refraction (Lorenz formula) is greater than that calculated, the differences being greater in the fumaroid compounds. (See *Abstr.*, 1895, ii, 149; this vol., ii, 135, 137.)

L. M. J.

Behaviour of Argon and Helium when submitted to the Electric Discharge. By J. NORMAN COLLIE and WILLIAM RAMSAY (*Proc. Roy. Soc.*, 1896, **59**, 257—270).—The experiments described fall into two classes: the first series relates to the distance through which electric sparks from an induction coil will strike through argon and through helium at atmospheric pressure, contrasted with the length of the spark gap in other gases, and also with the pressure at which the spark discharge changes into a ribbon-like discharge in different gases.

The second series, which was made with the object of determining how much of one gas is detectable in its mixture with another at

45

different pressures, deals with the spectra of gases in electrodeless vacuum tubes.

In the first series, it was found that with argon the distance traversed by the spark is considerably greater than with air, oxygen, or hydrogen; whilst with helium, the spark is capable of passing through most unusual distances. Pure gases having been prepared, the results were:—Oxygen, 23·0 mm.; air, 33·0 mm.; hydrogen, 39·0 mm.; argon, 45·5 mm.; helium, probably 250—300 mm. The discharge in the case of helium was a ribbon of flame of a blue colour, not showing the yellow D_3 line very brightly.

It was then discovered that the spark discharge changes to a ribbon discharge at some definite pressure with all gases, and the following determinations were made.

Gas.	Pressure of changes of character of discharge.
Air	73 or 74 mm.
Hydrogen.....	42 or 43 „
Oxygen.....	81 „
Carbonic anhydride	92 or 94 „
Cyanogen	23 „
Nitrogen	33 „
Carbonic oxide	49 „
Helium.....	1270 „

Helium, therefore, presents a behaviour different from all other gases. In short, a tube like those termed “Pflücker’s tubes,” need not be filled with helium at a low pressure, but exhibits all the phenomena of a vacuum tube at ordinary atmospheric pressure.

In the second series, experiments were performed with the view of ascertaining whether the spectrum affords an adequate test of the purity of gases.

The following table shows the quantities of different gases visible in the mixtures of them.

- (1) Helium in hydrogen, 33·0 per cent. of helium invisible at 2·61 mm.
 „ „ 10·0 per cent. of helium barely visible at the lowest pressures.
- (2) Hydrogen in helium, 0·001 per cent. of hydrogen visible at all pressures.
- (3) Nitrogen in helium, 0·01 per cent. of nitrogen almost invisible.
- (4) Helium in nitrogen, 10·0 „ of helium difficult to detect.
- (5) Argon in helium, 0·06 „ still visible at all pressures.
- (6) Helium in argon, 33·0 „ invisible at 2·62 mm.
 „ „ 25·0 „ 0·58 „
- (7) Nitrogen in argon, 0·42 „ 0·17 „
 „ „ 0·08 „ 0·18 mm. although just visible at 1·05 mm.
- (8) Argon in nitrogen, 37·0 „ barely visible at any pressure.
- (9) Argon in oxygen, 2·3 „ difficult to distinguish at 1·04 mm.

The effect of oxygen is to greatly decrease the luminosity of the argon spectrum. The reduction of pressure has no effect in intensifying the spectrum. J. F. T.

Temperature Coefficient of the Electromotive Force of Silver Cells. By JOHAN M. LOVÉN (*Zeits. physikal. Chem.*, 1896, 20, 456—460).—The energy relations in a galvanic chain are given by the equation $\pi\epsilon = E + \epsilon T \cdot d\pi/dT$, where π is the E.M.F., ϵ the electricity developed, and E the total energy of the change. The temperature coefficient $d\pi/dT$ may therefore be either positive or negative according as the total energy is less or greater than the electrical energy. Measurements were made in the chain, silver | silver chloride in potassium chloride solution | potassium nitrate solution | silver nitrate solution | silver, and similar chains with bromide and iodide. The current and E.M.F. were determined, and also the heat of precipitation of silver chloride (which is the chemical change of the process), as well as the temperature coefficient, which was in each case found to be negative. The value for $\epsilon T \cdot d\pi/dT$ agreed fairly well with the difference between the electrical energy, and the heat of precipitation, as indicated theoretically. L. M. J.

Sublimation Temperatures in the Cathode-Light Vacuum. By FRIEDRICH KRAFFT and H. WEILANDT (*Ber.*, 1896, 29, 2240—2245; compare this vol., ii, 464).—In the former experiments, it was found that substances of high melting point no longer melt in the vacuum of the cathode-light, but directly sublime. The following sublimation points are given:—Anthracene, 103—104°; phenanthrene, 95—96°; chrysene, 169°; pyrogallol, 105—106°; caffeine, 116°; alizarin, 153—155°; retene, 135°; salicylic acid, 75—76°; camphoric acid, 163—164°; theobromine, 156°. Antipyrine distills at 141—142°. Codeine boils at 179°.

The alkaloids were found to yield very pure products on distillation in the vacuum. Quinine boils at 170—180°; morphine at 191—193°. Indigo was found to sublime at 156—158° without decomposition; carbamide at 125°, and thiocarbamide at 98—99°. Uric acid did not sublime, but decomposed at 400°. J. F. T.

Solubility of Solids in Gases. By HENRYK ARCTOWSKI (*Zeits. anorg. Chem.*, 1896, 12, 413—416).—The author considers that in order to test the validity of the laws of solubility, the simplest cases should be first studied, in which the effect of the solvent is reduced to a minimum. The solution of a solid in a gas appears to be such a case, and the sublimation of a solid may be regarded as a case of a purely physical solution. L. M. J.

Sublimation Velocity of Mercury Haloid Salts. By HENRYK ARCTOWSKI (*Zeits. anorg. Chem.*, 1896, 417—426).—The velocities of sublimation of the halogen salts of mercury were determined by observing the loss of weight the salts experienced when kept at definite temperatures in a current of dry air. Mercuric chloride, bromide, and iodide, and mercurous chloride were examined, and curves constructed for temperature | loss of weight. The velocities of sublimation of the

three mercuric salts decrease as the molecular weight increases, whilst that of mercurous chloride is considerably less than even that of mercuric iodide, indicating probably a higher molecular weight, and the formula Hg_2Cl_2 , not HgCl . The curves for the three mercuric compounds closely resemble one another, differing only by a constant temperature difference, but the curve for calomel differs considerably from these. The velocity also appears to be dependent on the nature of the surface, and, for the same substance, decreases as the density increases. The velocities being measures of the vapour tension of the solid, may also be regarded as measures of the solubility of the solid in the gas (see preceding abstract).

L. M. J.

Sublimation Tension of Iodine. By HENRYK ARCTOWSKI (*Zeits. anorg. Chem.*, 1896, **12**, 427—430).—The sublimation tension of iodine at various temperatures has been previously determined at temperatures above 85° , and the author extends the observations to temperatures as low as 13° by measurement of the sublimation velocity. At 13° , this tension is only 0.1 mm. The velocity at a pressure of about 15 mm. was also determined, and, as expected, found to be considerably greater than at the ordinary atmospheric pressure.

L. M. J.

Determination of the Freezing Point of Dilute Aqueous Solutions. By A. PONSOT (*Compt. rend.*, 1896, **113**, 189—192).—The author discusses certain of the conditions under which the observed reduction of the freezing point of dilute solutions accurately represents the true reduction, having regard to the effects of the concentration of the solution, superfusion, the rate of cooling, and the velocity of the agitator. The general conclusion is that the most accurate result is obtained when the value of the rate of cooling (V_1) is zero (compare Abstr., 1894, ii, 342).

C. H. B.

Influence of Chemical Affinity on Solubility. By ST. TOLLOCZKO (*Zeit. physikal. Chem.*, 1896, **20**, 412—416).—Although the two components of a racemate show identical chemical properties, it was considered possible that a difference in solubility might exist if the solvent were itself an active compound. To determine whether this was so, a racemate was obtained in solution equilibrium with water and an active solvent, and then the solutions examined optically, to test for excess of either constituent. In the first case, racemic acid was used, the solvents being water and lævo-amylic alcohol, and in the second case mandelic acid, with ether and an aqueous solution of levulose. In both cases negative results were obtained, no excess of either active constituent entering into either solvent.

L. M. J.

The Lowering of Solubility. By ST. TOLLOCZKO (*Zeits. physikal. Chem.*, 1896, **20**, 389—412).—According to Nernst's law (Abstr., 1890, 1368), the relative lowering of the solubility of a solvent in a second liquid caused by the addition of a foreign substance is equal to the ratio of the number of dissolved molecules of the foreign

substance to the number of molecules of the solvent. The author endeavoured to prove the law by determining the effect of various organic compounds, insoluble in water, on the solubility of ethylic ether in water. The expression has to be somewhat altered, owing to the solubility of water in the ether, and an expression allowing for this is deduced. The experimental details are recorded, and the results for the molecular weight, calculated on the assumption of the law, are given in the accompanying table, in which the concentration is given in grams per 100 grams of pure ether, and the highest and lowest concentrations alone are recorded.

	Concentration 1.	Concentration 2.	Mol. wt. (1).	Mol. wt. (2).
Benzene	1.77	13.3	81.0	83.0
Toluene	1.77	13.25	87.0	85.0
Xylene	1.67	18.0	103.0	110.0
ψ -Cumene	2.98	—	116.0	—
Diamylene	1.15	20.3	134.0	149.0
Thymol	1.75	23.25	135.0	133.0
Borneol	1.93	4.17	139.0	156.0
Menthol	1.30	21.15	140.0	156.0
Chloroform	1.10	20.15	109.5	122.5
Carbon bisulphide	11.27	—	85.0	—

The results prove the validity of the law and its use for the determination of molecular weights, even at comparatively high concentrations. The solubility of ether was also determined at numerous temperatures, the value in grams of ether per gram of water being: 13°, 0.08930; 15°, 0.08399; 17°, 0.07955; 19°, 0.07494; 21°, 0.06948. The experiments also indicate the great effect of small quantities of impurities if the ether is only in small excess, the true values being only obtained when the excess of ether is great. L. M. J.

Influence of Pressure on Solubility. By ED. VON STACKELBERG (*Zeits. physikal. Chem.*, 1896, **20**, 337—358).—The author first investigates theoretically from the thermodynamical standpoint, expressions for the effect of pressure on solubility. A relation connecting the pressure and temperature effects is first established, and then a formula is deduced, which is independent of the temperature coefficient. By means of a Caillottet's pump, saturated solutions of sodium chloride, alum, and ammonium chloride were obtained at a pressure of 500 atmos., and small quantities were withdrawn and analysed. The pressure coefficients were hence obtained, and compared with those deduced theoretically. The results obtained for the three salts are as follows, the value d/x being the increase in milligrams per gram of solution for 100 atmos.

Salt.	d/x found.	d/x calc.
Sodium chloride	+1.2	+3.2
Ammonium chloride.....	-2.8	-3.7; -2.5
Alum	+6.7	+13.2

L. M. J.

Etherification. By HEINRICH GOLDSCHMIDT (*Ber.*, 1896, 29, 2208—2216).—The author, having previously suggested (this vol., i, 229) that the acceleration of the speed of etherification which occurs on adding a strong acid to an alcoholic solution of an acid is due to the presence of hydrogen ions, now brings further evidence in support of his view. If the speed of etherification be dependent on the extent to which the catalysing acid is dissociated, the addition of a salt of the latter should bring about a decrease in the velocity of etherification. It is found that, by adding paratoluidine picrate to an alcoholic solution of phenylacetic acid, picric acid being also added to serve as a catalyst, etherification is greatly retarded; the speed of etherification decreases as the quantity of paratoluidine picrate added is increased. The velocity constant k , calculated from the equation representing a monomolecular reaction, such as that supposed to occur during etherification, decreases gradually as the time increases, the decrease being much less in the experiments in which paratoluidine picrate is used than in those in which no salt is added. In the case of the latter, the decrease is caused by the water continually produced, but the retarding effect of the water is partially compensated when toluidine picrate is present, because the water partially decomposes the salt and so increases the available quantity of free acid.

An alcoholic solution of trichloroacetic acid slowly changes into ethylic trichloroacetate at ordinary temperatures; the author has studied the rate of change at 25°, and finds that, considering the reaction as a monomolecular one, the constant k decreases continuously with the time. The constant k decreases very slowly if the action be calculated as a bimolecular one, so that the etherification must, in this case, be the result of autocatalytic action, the reaction between the acid and alcohol being due to the presence of hydrogen ions resulting from the dissociation of the acid. The same result is obtained on recalculating Petersen's numbers (*Abstr.*, 1895, ii, 258) representing the velocity of etherification of formic acid dissolved in methylic alcohol.

It follows that etherification occurring, with or without the addition of a catalysing acid, is primarily caused by the activity of the hydrogen ions present, so that the various theories premising intermediate stages of the reaction in etherification are now unnecessary.

W. J. P.

Indirect Etherification. By EMIL PETERSEN (*Zeits. physikal. Chem.*, 1896, 20, 331—333).—The author considers that, although Tafel's explanation regarding the action of small quantities of hydro-

gen chloride in "indirect etherification" (this vol., ii, 470) is probably correct, it does not vitiate the availability of the method in those cases where it is desirable (Abstr., 1895, ii, 258). L. M. J.

Relation between the Colours of Atom, Ion, and Molecule.

II. By M. CAREY LEA (*Zeits. anorg. Chem.*, 12, 340—352; compare Abstr., 1895, ii, 441; this vol., ii, 594).—(1) Coloured inorganic substances composed of colourless ions yield colourless solutions; for example, take the colourless solutions of mercuric iodide in alcohol, and of antimony pentasulphide in alkaline sulphide solutions. This shows that in solution the ions are so far separated that their vibrations do not mutually influence each other. (2) There is no relation between the colour of a molecule and those of its constituent ions. Two colourless ions may give a coloured molecule, as in the case of bromine, and of silver sulphide; and coloured ions may give a colourless molecule, as in the case of the white metal nickel, the ions of which are green, or a molecule of a different colour, as in the case of red copper, the ions of which are blue. (3) The change of colour of the indicators used in acidimetry is not due to dissociation, for the colour of the alkaline solution, in which the dissociated sodium salt of the colour acid is supposed to exist, persists after the water has been evaporated off, and the possibility of dissociation thus removed. (4) The systems of arrangement of the elements proposed by Thomsen (Abstr., 1895, ii, 491; this vol., ii, 16) and de Boisbaudran (Abstr., 1895, ii, 440) have much in common with that of the author (Abstr., 1895, ii, 441). (5) The ions are not absolutely free in solution, but are subject to some kind of mutual restriction; for example, the chlorine ions of hydrochloric acid are unable to convert the ferrous ions of a solution of ferrous chloride into ferric ions until the hydrogen ions, by which they are accompanied, are removed by an oxidising agent. C. F. B.

The Origin of Dalton's Atomic Theory. By HEINRICH DEBUS (*Zeit. physikal. Chem.*, 1896, 20, 359—376).—The author contests several conclusions of Roscoe and Harden, published in the *New Views of Dalton's Atomic Theory*. He sums up his own conclusions as follows. (1) That in 1801, Dalton, from physical considerations, was led to the hypothesis that equal volumes of gases under normal conditions contain equal numbers of molecules, that is, $M/d = k$. (2) That it is highly probable that this hypothesis, together with his observations on the oxides of nitrogen, led him to formulate his atomic theory. (3) Atomic views led Dalton, in 1805, to abandon his hypothesis $M/d = k$. (4) Avogadro was probably aware of Dalton's views, and borrowed his hypothesis. L. M. J.

Twin-Elements. By RICHARD LORENZ (*Zeits. anorg. Chem.*, 12, 329—339).—The following 14 pairs of twins are said to exist among the elements, by twins being understood two elements with generally similar properties, and of which the atomic weights do not differ by more than 1.4 (usually about 1): B-C, Na-Mg, Al-Si, P-S, K-Ca, V-Cr, Mn-Fe, Ni-Co, Se-Br, Pd-Ag, Sn-Sb, I-Te, Ta-W, Pb-B

It is also noticed that the atomic weight of a member of one twin pair differs from that of the corresponding member of the next twin pair by some multiple of 4 (the atomic weights being taken to the nearest integer), and that the other elements, which do not form pairs, also obey this law, so that these elements may be taken each as representing a twin pair, the other member of which is not known; exceptions are H, Be, N, Zn, Ga, Rb, Y, Zr, Nb, In, Cs, Ba, Ir, Au, and certain rare-earth metals, the atomic weights of which have not as yet been accurately determined. It is pointed out that, according to this system, tellurium should have a greater atomic weight than iodine, which is in accordance with the latest determinations.

C. F. B.

Simple Method of Reducing Weight in Air to Weight in a Vacuum. By FRITZ SALOMON (*Zeit. angew. Chem.*, 1896, 529—531).—The author calls attention to the fact that chemists generally neglect to convert weight in air into weight in a vacuum, and describes a modification, suitable for placing in a balance case, of his "barothermometer" (*Zeit. angew. Chem.*, 1893 and 1894), an instrument which shows the weight of a litre of air at the atmospheric temperature and pressure at the time of observation.

L. DE K.

Inorganic Chemistry.

Atomic Weights of Oxygen and Hydrogen. By EDWARD W. MORLEY (*Zeits. physikal. Chem.*, 1896, 20, 417—455).—The densities of the two gases having been previously determined (this vol., ii, 518 and 595), the question of the atomic weights was next considered.

The first method was similar to that of Leduc (Abstr., 1892, 1388), that is, was dependent on the determination of the density of the mixed gases evolved by the electrolysis of an alkaline solution. One point observed in the researches was the capability which air possesses of creeping between the mercury and the glass into the eudiometer if the mercury is not covered by a layer of sulphuric acid. In all the analyses of the electrolytic gas, the hydrogen was found to be present in slight excess, the average for the series being 0.000293 (= excess / total gas). This has to be allowed for in the calculation, and was probably overlooked by Leduc. The density of the mixed gases was thus obtained as $D = 0.535510 \pm 0.000010$ (gram / litre). The ratios of the volumes of oxygen and hydrogen in the mixture were then calculated on the assumption of Van der Waals' equation, and found to be 1 : 2.00357, yielding the ratio for the combined volumes = 1 : 2.00269.

The second method was by means of the synthesis of water by the combination of weighed quantities of the gases. The oxygen was weighed as in the density determinations, and the hydrogen by the loss of a charged palladium tube, and the uncombined residue was in all cases eudiometrically analysed. The mean value

for the ratio of the atomic weights obtained from the weights of the two gases was 15·8792, and from the weights of hydrogen and water 15·8785, whilst that calculated by the first method is also 15·879, which is, moreover, the mean value of the results of Dittmar and Henderson (15·866, 15·868), Cooke and Richards (15·869), Leduc (15·881), Rayleigh (15·89), and Noyes (15·897). The value $O = 15·879$ is hence at present the most probable value for the atomic weight.

L. M. J.

Replacement of the Chlorine in Chlorides of Non-Metals and Metalloids by Bromine and Iodine. By H. LLOYD SNAPE (*Chem. News*, 1896, **74**, 27—29).—In many experiments, various non-metallic chlorides were heated in sealed glass tubes in a paraffin bath with excess of the metallic haloid salt, the objects being to heat the dry materials out of contact with the air, to watch for any decomposition and to adjust the temperature accordingly, and to avoid inconvenience arising from the presence of any undecomposed non-metallic chloride in the final product. In this way, with potassium bromide, phosphorus trichloride was apparently unchanged at 200—220°, carbon tetrachloride (like silicon tetrachloride) was but little attacked at 200°, whereas sulphur monochloride at 200—220° and arsenic trichloride at 180—220° were partially converted into bromides. With potassium iodide, both sulphur monochloride and carbon tetrachloride were more completely decomposed, the former even at ordinary temperatures, the latter at 200°, but yielded only mixtures of sulphur and iodine, and carbon and iodine respectively, whilst phosphorus trichloride at 200°, arsenic trichloride at 240°, and antimony chloride at 200° were readily converted into their iodides. A repetition of Guthrie's experiment with sulphur monochloride and ethylic iodide also yielded a mixture of sulphur and iodine. Antimony trichloride too could be converted into antimony tribromide by passing the vapour over a long layer of potassium bromide heated to a temperature sufficiently high to decompose the double salt.

D. A. L.

Nitrosodisulphonic acid and its Salts. By PAUL SABATIER (*Compt. rend.*, 1896, **123**, 255—258).—A solution of nitrososulphonic acid or sodium nitrite in sulphuric acid is reduced not only by cuprous and ferrous salts (this vol., ii, 599, 622), but also by a large number of other substances, with production of the blue nitrosodisulphonic acid. Mercury acts very rapidly, but also readily decomposes the nitrosodisulphonic acid. Finely divided silver, tin, and aluminium behave in the same way, and so also do cadmium, antimony, and lead, although much more slowly. Zinc, even in powder, bismuth, chromium, uranium, sulphur, phosphorus, nickel, arsenic, thallium, and magnesium react more or less readily, but do not produce the blue compound. Selenium and tellurium behave as with sulphuric acid alone. Arsenious anhydride, antimonious, manganous, and stannous oxides, mercurous and chromous chlorides, carbon bisulphide, and arsenic, bismuth, tin, and zinc sulphides, potassium ferrocyanide, carbamide, and oxalic, tartaric, and citric acids give no distinct result. On the other hand, the blue product is

readily produced by zinc phosphide or arsenide, and by barium hypophosphite, less readily by lead sulphide and stannous chloride. Alcohol, ether, glycerol, and even acetic acid will produce a blue ring if added to the nitrososulphonic acid solution.

The salts are more stable than the acid (*loc. cit.*), and if a cupric salt or a ferric salt is dissolved in the nitrososulphonic acid solution, and the reducing agents are then allowed to act, the colour produced is much more intense, and it is observed with substances such as arsenic and zinc sulphides, bismuth, zinc powder, &c., which do not seem to act under ordinary conditions.

Sulphurous anhydride reduces the nitrosulphonic acid only in presence of water. The blue compound is formed, for instance, if sulphurous anhydride is dissolved in sulphuric acid diluted with one-third of its volume of water, and this liquid is added to an equal volume of the nitrosulphonic acid solution. The copper salt is formed by adding copper nitrite to a solution of sulphurous anhydride in sulphuric acid containing a small quantity of water.

When nitric oxide is passed into a solution of cupric sulphate in sulphuric acid, the blue compound is formed as Desbassins and Richmond have observed. Nitrosulphonic acid is formed as well as cupric nitrosodisulphonate, $3\text{NO} + \text{CuSO}_4 + \text{H}_2\text{SO}_4 = \text{NO}(\text{SO}_3)_2\text{Cu} + 2\text{NO}_2\text{SO}_3\text{H} + 2\text{H}_2\text{O}$, and on adding a cuprous salt a further quantity of the cupric nitrosodisulphonate is produced. Ferric sulphate behaves like cupric sulphate. The red-violet compound is produced still more readily when the nitric oxide is passed into a solution of ferrous sulphate in sulphuric acid, part of the ferrous salt being oxidised. The nitric oxide has no action on sulphuric acid alone, nor on solutions of chromic or manganic sulphate in the acid.

C. H. B.

Preparation of Selenic acid. By R. METZNER (*Compt. rend.*, 1895, 123, 236—238).—When excess of potassium permanganate is added to a solution of selenious acid, complete oxidation takes place, the products being selenic acid and potassium selenate, which remain in solution, and manganese sesquioxide, which is completely precipitated if the solutions are dilute. After removal of the manganese oxide, the potassium can be precipitated by means of hydrofluosilicic acid.

A better method is to employ permanganic acid, obtained from pure barium permanganate. The solutions should be dilute, and it is best to add the selenious acid to the permanganic acid. After removal of the manganese oxide and concentration of the wash water, a small quantity of permanganic acid is added to oxidise the trace of selenious acid that remains and to precipitate a small quantity of manganese that has dissolved. Sometimes it is necessary to heat the liquid to boiling, but the manganese oxide separates immediately on the addition of a drop of selenious acid solution. Finally permanganic acid is added until the liquid shows a persistent pink tinge in a column 20 cm. thick, and the liquid is concentrated, preferably under reduced pressure. An acid can be obtained, which corresponds almost exactly with the composition H_2SeO_4 . C. H. B.

Metallic Compounds of Triphosphoric acid. By MARTIN STANGE (*Zeits. anorg. Chem.*, 1896, **12**, 444—463).—Sodium triphosphate, $\text{Na}_5\text{P}_3\text{O}_{10} + 8\text{H}_2\text{O}$, is obtained by heating sodium pyrophosphate with sodium metaphosphate, or better, sodium pyrophosphate (111·8 parts) with phosphate (73·1 parts) at a bright red heat for 20—30 minutes. The melt becomes warm when dissolved in water, and part of the triphosphate is decomposed into pyro- and meta-phosphates. The salt is obtained pure by adding water to the mother liquors of the melt, which solidify on cooling, and either separating the salt by filtration or by spreading it on a porous plate. The product is a fine powder consisting of four-sided leaflets, and is quite free from metaphosphoric acid. It is decomposed by heat, acids, and bases, as already described by Schwarz (Abstr., 1895, ii, 445). When treated with strong ammonia, it forms a white emulsion, and then an oil is precipitated, which is a concentrated solution of metaphosphate. Schwarz states that orthophosphate is formed by the action of ammonia; but the author was unable to obtain orthophosphate even by boiling the mixture.

The properties of cobalt, nickel, and zinc triphosphates, $\text{CoNa}_3\text{P}_3\text{O}_{10} + 12\text{H}_2\text{O}$; $\text{Zn}_2\text{NaP}_3\text{O}_{10} + 9\frac{1}{2}\text{H}_2\text{O}$, have already been described by Schwarz. He obtained the cobalt and nickel salts, however, only after the mixture had been allowed to remain some time; a similar result was obtained by the author when working with sodium triphosphate containing metaphosphate, but when pure materials were used, a precipitate was at once formed.

Ferrotrisodium triphosphate, $\text{FeNa}_3\text{P}_3\text{O}_{10} + 11\frac{1}{2}\text{H}_2\text{O}$, is obtained by adding sodium triphosphate to a solution of ferrous sulphate. The solution, after filtration, deposits the salt in slender, silky, white needles. It is stable when dry, but in contact with water rapidly oxidises and forms a brown syrup, which probably consists of a basic salt. It dissolves in nitric acid, and, on warming, is converted into ferric pyrophosphate with a very violent evolution of nitric oxide. It is dehydrated only by heating to the melting point, and ferrous oxide is then deposited. The author was unable to obtain the corresponding ferric salt, probably because it is very easily soluble in water, and thereby undergoes decomposition.

Magnesium trisodium triphosphate, $\text{MgNa}_3\text{P}_3\text{O}_{10} + 13\text{H}_2\text{O}$, is obtained by adding a solution of magnesium chloride to one of sodium triphosphate until a permanent precipitate begins to form; this is quickly redissolved by the addition of sufficient triphosphate, and the salt then at once commences to separate. It crystallises in very slender needles, is decomposed by exposure to air, losing water of crystallisation, and, when heated, intumesces like borax, and melts at a red heat to a clear glass easily soluble in acids.

Manganese trisodium triphosphate, $\text{MnNa}_3\text{P}_3\text{O}_{10} + 12\text{H}_2\text{O}$, is obtained by mixing a solution of manganese sulphate with sodium triphosphate. It crystallises in slender, white prisms, loses its water of crystallisation only when heated to redness, and then melts to a colourless glass which is easily soluble in sulphuric acid.

Tricopper sodium pyrophosphate, $\text{Cu}_3\text{Na}_2\text{P}_2\text{O}_7 + 10\text{H}_2\text{O}$, is obtained by mixing a solution of sodium triphosphate with copper sulphate

until a permanent precipitate is obtained. It is a white, crystalline powder, quite insoluble in water, and when heated becomes blue, green, then yellowish-green, and sinters at a high temperature. Even after heating, it is soluble in nitric and hydrochloric acids.

Cupric trisodium triphosphate, $\text{CuNa}_3\text{P}_3\text{O}_{10} + 12\text{H}_2\text{O}$, is obtained by mixing sodium triphosphate and copper sulphate in the theoretical proportions. It crystallises from the solution, after 1 to 2 days, in lustrous, bluish-green prisms. When heated, it melts in its water of crystallisation, and at a red heat is converted into a glass which, when hot, is yellow, when cold, bluish-green, and is easily dissolved by acids.

Lead triphosphate-sodium pyrophosphate, $\text{Pb}_3\text{Na}_4\text{P}_5\text{O}_{27} + 10\text{H}_2\text{O}$, is obtained by adding a neutral solution of lead nitrate to a solution of sodium triphosphate until a permanent precipitate is produced, and then dissolving the latter by the addition of more triphosphate. It crystallises in yellowish nodules, and melts, when heated, to a colourless glass, which is easily soluble in nitric acid. An amorphous lead salt is obtained by employing an excess of lead nitrate; it has not, however, a constant composition, and contains sodium which cannot be eliminated by prolonged washing. When the salts are allowed to react with one another for some time, the analysis of the product approaches that of lead triphosphate. From dilute solution, however, and when the precipitate is at once separated, the product appears to be lead pyrophosphate contaminated with metaphosphate. The filtrate from the precipitate contains lead and phosphoric acid, so that apparently an excess of lead salt decomposes the triphosphate.

Trisilver sodium pyrophosphate.—The action of silver nitrate on sodium triphosphate is very similar to that of lead nitrate, and complicated pyrophosphates are obtained, which the author was unable to isolate. A salt of the composition $\text{Ag}_3\text{NaP}_2\text{O}_7 + \frac{1}{2}\text{H}_2\text{O}$, which is probably formed in the above reaction, is obtained by treating a saturated solution of sodium pyrophosphate with silver nitrate, when it is precipitated as a heavy, crystalline powder, together with amorphous silver pyrophosphate. When strongly heated, it melts to a brown liquid, which, on cooling, forms a lemon yellow, crystalline mass containing orthophosphate.

Chromium salts give no precipitate with triphosphate, but with a mixture of molecular proportions of meta- and pyro-phosphates, a green precipitate is obtained. With manganese salts, triphosphates yield a crystalline precipitate of triphosphate, whilst with the mixed phosphates an amorphous precipitate is formed, and only after remaining some weeks, a small quantity of crystalline manganese trisodium triphosphate. Cadmium salts give no precipitate with a solution of triphosphate, and with a solution of the mixed phosphates, a precipitate of small crystals. From the above results, the author concludes that the triphosphates are chemical compounds, and not double salts of pyrophosphate with meta-phosphoric acid.

E. C. R.

Artificial Production of Diamonds. By HENRI MOISSA (*Compt. rend.*, 1896, **123**, 206—210).—Iron was carburised and fused in the electric furnace and allowed to fall into mercury 10 cm.

deep covered with water 20 cm. deep. The irregular shaped granules thus obtained were saturated with carbon, but contained none of high sp. gr.; the spheres or ellipsoids formed at the same time contained, however, both black diamonds and transparent diamonds, some of which, although microscopic, showed remarkable regularity of crystalline form.

Larger masses of the fused carburetted iron were allowed to fall into water and mercury at the bottom of a pit shaft 32 metres deep, but the conditions of the experiment were not favourable to the production of spherical masses of iron. It was observed that when the falling globules touched the tub containing the mercury, or came in contact with the earth they broke up, with a flame, into scintillating globules, the change being accompanied by a report like that of a rifle. It was also observed that even during the short time occupied by the fall, the temperature of the globules was materially reduced.

In other experiments, the fused carburetted iron was run into a small cylindrical cavity in a large mass of iron or copper. Under these conditions, the fused metal is very rapidly cooled, and diamonds are obtained mixed with graphite, but the yield is not very satisfactory.

C. H. B.

Black Diamonds. By HENRI MOISSAN (*Compt. rend.*, 1896, **123**, 210—211).—The black matter, or so-called black diamond, included in transparent diamonds from Brazil, is composed of a variety of carbon different from diamond. When such diamonds are powdered and heated in oxygen at a temperature 200° below the ignition point of the diamond, the black matter burns away with production of carbonic anhydride, and the residual diamond is quite white.

C. H. B.

Homogeneity of Argon and Helium. By WILLIAM RAMSAY and J. NORMAN COLLIE (*Compt. rend.*, 1896, **123**, 214—216, and also *Nature*, 1896, **54**, 546).—In each case the gas was allowed to diffuse through a small tube of porous earthenware into a vacuum, and was submitted to several successive fractionations in this way. Direct experiment showed that the process permits of the separation of helium from hydrogen, and carbonic anhydride from oxygen, and that by observing the rate of descent of a column of mercury connected with the apparatus, a fairly accurate determination of the sp. gr. of a gas may be made.

In the case of argon, several fractionations resulted in two portions of the gas being obtained of sp. gr. 19.93 and 20.01 respectively, and it follows that little or no separation is effected.

In the case of helium, on the other hand, the gas was separated into two portions of sp. gr. 1.874 and 2.133 respectively, and repeated fractionation of each of these portions failed to alter these figures. Determinations of the refractive indices of the two gases by Lord Rayleigh gave for the lighter 0.1350 (air = 1), and for the heavier 0.1524, the two values being almost exactly proportional to the sp. gr. of the gases. Both fractions of helium gave absolutely the same spectrum. It is, therefore, impossible to say that one fraction is a mixture, whilst the other is homogeneous.

Having regard to the fact that the spectra of the two gases are identical, that the refractive indices of known gases of different chemical composition are not proportional to their sp. gr., and that it is improbable that there should be two different gases with nearly the same sp. gr., the authors suggest that in their experiments they may have separated light molecules of helium from heavy molecules of helium. C. H. B.

Quick Nitrogen Absorbent for the Liberation of Argon and the Manufacture of Metallic Lithium. By HENRY N. WARREN (*Chem. News*, 1896, **74**, 6).—Dry lithium hydroxide is heated in a tubulated iron retort, metallic magnesium being added in small pieces from time to time through the tubulure; metallic lithium distils over. The carbonate may be used, but then the metal is contaminated with carbide, which evolves acetylene in contact with water.

A material which absorbs nitrogen with great avidity is obtained by the reduction, in an atmosphere of hydrogen at as low a temperature as possible, of a mixture of magnesium powder with calcium or barium hydroxide, saturated with a strong solution of lithia. D. A. L.

Alloys. By HENRI GAUTIER (*Compt. rend.*, 1896, **123**, 172—174).—The author has determined the melting points of a number of alloys with the object of ascertaining whether there is a group of alloys containing two metals which are not isomorphous, but which form an alloy isomorphous with one of them, and are, therefore, analogous to ammonium ferric chloride, sodium silver chloride, or calcium sodium sulphate. In the following table, the compositions of the alloys are given in per cents. of the less fusible constituent.

Cd-Ag. M. p.	Zn-Ag. M. p.	Sn-Ag. M. p.	Sb-Ag. M. p.	Cu-Ni. M. p.
0·0 322°	0·0 433°	0·0 232°	0·0 632°	0·0 1050°
4·0 355	6·25 465	4·86 221	5·0 613	0·5 1045
10·6 422	30·0 595	16·66 312	10·0 590	20·0 1250
21·75 525	52·17 695	25·0 355	25·0 560	33·33 1310
36·23 660	58·0 715	33·33 390	33·33 540	50·0 1340
42·0 710	62·0 690	40·0 430	50·0 495	55·55 1370
51·0 755	72·50 695	50·0 475	55·0 482	66·66 1400
60·16 805	76·60 730	58·82 535	60·0 492	100·0 1450
68·65 840	89·54 870	66·66 600	66·6 525	— —
77·63 880	94·24 910	74·62 682	75·0 583	— —
86·1 925	100·0 954	83·33 815	83·33 750	— —
91·8 945	— —	90·90 900	90·9 885	— —
95·5 950	— —	100·00 954	100·0 954	— —
100·0 954	— —	— —	— —	— —

In the case of the silver-cadmium, silver-zinc, and silver-tin alloys, the variations in the melting points are not analogous to those observed in the case of the salts previously referred to. Further, whilst, as a rule, the addition of a small quantity of metal to another more fusible metal lowers the melting point, the reverse is the case with silver and cadmium, and silver and zinc. The melting points of

tin and bismuth are raised by the addition of small quantities of antimony, which is isomorphous with bismuth. The immediate raising of the melting point of the more fusible of the two constituents of the alloy seems to be intimately related to the phenomena of isomorphism.

The curve of the melting points of the copper-nickel alloys indicates the formation of a compound, CuNi , whilst the corresponding curve for the silver-antimony alloys indicates that they are simply mixtures.

C. H. B.

Magnesium Cobaltite. By E. DUFAU (*Compt. rend.*, 1896, 123, 239—240).—When an intimate mixture of 150 grams of cobaltic oxide, Co_2O_3 , and 75 grams of magnesium oxide is heated for 10 minutes in the electric furnace with an arc from 300 ampères and 70 volts, *magnesium cobaltite*, CoO_3Mg , is obtained as a very deep, garnet-red, crystalline mass of sp. gr. 5.06 at 20° . Its hardness is between 4 and 5. The cobaltite is dissolved by hydrofluoric acid, by hydrochloric acid with evolution of chlorine, and by nitric and sulphuric acids with evolution of gas, and it is also decomposed and partially dissolved by ammonia. Oxygen is without action on it at a red heat, but sulphur converts it into cobalt sulphide at a lower temperature. Chlorine attacks it with production of cobaltous chloride, which sublimes, and bromine behaves similarly, but iodine seems to have no action. Dry hydrogen fluoride and dry hydrogen chloride also decompose it readily, but fused oxidising agents have no action on it.

C. H. B.

Electro-Chemical Method of preparing Metallic Hydroxides.

By RICHARD LORENZ (*Zeits. anorg. Chem.*, 1896, 12, 436—441).—A bath of potassium or sodium chloride, sulphate, or nitrate, dissolved in water, is used according to the ease with which the several hydroxides are formed in these solutions. The cathode consists of a platinum plate, and the anode of a plate of the metal whose hydroxide is to be prepared. The electrolyte is continually stirred, and the metallic hydroxide is obtained as an insoluble precipitate. An anode of copper in a solution of potassium chloride, gives a yellowish-red precipitate of cuprous hydroxide, and in a solution of potassium nitrate, a blue precipitate of cupric hydroxide. Silver, magnesium, zinc, cadmium, aluminium, lead, manganese, and iron, when treated by this method, are easily converted into their hydroxides. Mercury gives no precipitate when treated in a bath of potassium chloride, calomel being formed; in a bath of potassium nitrate, a black precipitate is obtained. Thallium, when treated in baths of the potassium salts, becomes covered with a coat of suboxide, and a brown precipitate of thallium hydroxide is very gradually formed. Tin, when treated in a bath of chloride, sulphate, or nitrate, yields orthostannic acid, which, by this method, is easily obtained pure. Antimony and bismuth, treated by this method, become coated with a grey skin, and no hydroxides are formed. Nickel, in a bath of the nitrate, becomes quickly coated with a black skin; in a bath of the chloride, the green hydroxide is very easily obtained.

The method is applicable to the preparation of hydroxides which are insoluble in water; hydroxyl ions and metal ions are formed in equivalent proportions, and therefore the hydroxide is obtained in neutral solutions, and this is a great advantage over the chemical method, where it is necessary to wash the hydroxides free from alkali. Since the precipitated hydroxides are formed in the solution, and not at the cathode or anode, the latter do not become foul, and a large quantity of the hydroxide can be prepared with the same strength of current and solution. It is important that the anodes should be made of pure metal, as it is the impurities in the metal alone which can contaminate the hydroxides prepared by this method. E. C. R.

Electro-Chemical Method of preparing Metallic Sulphides.

By RICHARD LORENZ (*Zeits. anorg. Chem.*, 1896, **12**, 442—443).—The method is similar to that described in the preceding abstract for the preparation of metallic hydroxides. A cathode of copper sulphide is employed, and an anode of the metal whose sulphide is to be prepared. The bath consists of a solution of potassium or sodium chloride, nitrate, or sulphate. Copper, silver, cadmium, tin, lead, iron, and nickel sulphides are easily obtained. The method is evidently of general application, and is very convenient, as the metallic sulphides are formed in neutral solution and without using hydrogen sulphide or alkali sulphides. E. C. R.

Action of Hydrogen Sulphide on Solutions of Cupric Salts.

By BOHUSLAV BRAUNER (*Chem. News*, 1896, **74**, 99; compare Coppock, this vol., ii, 562).—Investigations have been made on the complete precipitation with a slow or rapid current of hydrogen sulphide, of aqueous solutions of cupric sulphate or chloride under varying conditions of dilution, acidity, and of temperature. The resulting precipitate, greenish-black or dark olive green in colour, was washed thoroughly and successively with hydrogen sulphide solution, alcohol, carbon bisulphide, alcohol, and ether, the air being rigorously excluded throughout by means of carbonic anhydride. The washed and unwashed precipitates have been analysed; the latter always consisted of copper, combined sulphur, and free sulphur, whilst the former was neither simply Cu_3S_2 nor CuS , but apparently contained varying proportions of CuS and Cu_2S . The exact conditions under which the larger proportion of one or the other is produced are not yet known, and are to form the subject of future experiments. It is suggested that the formation of sulphonyl-compounds of copper may have something to do with the reaction. D. A. L.

Mercuric Oxy-salts. By RAOUL VARET (*Compt. rend.*, 1896, **123**, 174—176).—Raoult and Guinchant have shown that mercuric oxy-salts do not exist in their solutions in the form of basic salts, and the author has endeavoured to determine whether they exist as normal or acid salts. Berthelot has shown that the thermal effect of the substitution of one metal for another in a saline solution is equal to the difference between the respective heats of formation of the initial and final compounds, and, on the other hand, Andrews, and Favre and

Silberman have shown that the amount of heat developed by the substitution of one metal for another in a saline solution is independent of the nature of the acid radicle. Berthelot's determinations, however, prove that this law does not hold good for mercuric chloride, bromide, or cyanide.

On the other hand, Berthelot's determinations show that in a solution of the acetate, the displacement of potassium by mercury develops +164.9 Cals.; the determinations of Berthelot and of the author show that in solutions of the picrate a similar displacement likewise develops +164.9 Cals. In the case of the nitrate, the displacement develops +165.0 Cals., and it follows that mercuric oxy-salts obey the law of thermochemical moduli, and that the nitrate exists in solution as the normal salt.

According to Berthelot, the heat of formation of potassium hydrogen sulphate, dissolved in dilute sulphuric acid, is -2.6 Cals. less than the heat of formation of the normal sulphate. The author has found that the heat of formation of mercuric sulphate, dissolved in dilute sulphuric acid, is +170.0 Cals., and hence the displacement of potassium by mercury in such a solution will develop +165.0 Cals., exactly as in the case of other mercuric oxy-salts. It follows that mercuric sulphate, dissolved in excess of dilute sulphuric acid, is present in the form of a hydrogen salt, strictly comparable with the corresponding sodium and potassium salts.

C. H. B.

Artificial Dendrites. By HENRYK ARCTOWSKI (*Zeits. anorg. Chem.*, 1896, **12**, 353—357).—Solutions of mercuric chloride, of concentration varying from 10—0.1 per cent., were left for three months in contact with marble at 39°. The oxychloride, $\text{HgCl}_2 \cdot 4\text{HgO}$ (Abstr., 1895, ii, 393), separated in definite crystals from the stronger solutions; in more or less parallel, but slightly interlacing plates, from the solutions of medium strength, the plates being seen under the microscope to be built up of small cubes; and in dendritic growths, precisely resembling those of native copper, from the weaker solutions. That better crystals are got from the stronger solutions is correlated with the fact that the oxychloride in question is more soluble in these solutions; it is quite insoluble in pure water.

C. F. B.

Mercurous Nitrite. By P. C. RAY (*Zeits. anorg. Chem.*, 1896, **12**, 365—374).—This substance, $\text{Hg}_2(\text{NO}_2)_2$, is obtained by diluting yellow nitric acid, of sp. gr. 1.41, with 3 parts of water, and allowing it to remain for one or two days, best at a temperature of about 30°, in contact with a large excess of mercury; the nitrite is deposited on the surface of the metal in the form of yellow needles. It is decomposed but slowly by dilute sulphuric acid in the cold, nitrous fumes being evolved; boiling with a large excess of water decomposes it to the extent of about 78 per cent. into mercury and mercuric nitrite. The author discusses the bearing that the formation and properties of mercurous nitrite have on the constitution of nitrites and the action of metals on nitric acid; he thinks that in it the metal is directly united to nitrogen, as in the nitrites of silver, copper, and bismuth.

C. F. B.

Lanthanum Carbide. By HENRI MOISSAN (*Compt. rend.*, 1896, 123, 148—151).—Lanthanum oxide is easily reduced by carbon in the electric furnace, although the temperature required is somewhat higher than in the case of cerium oxide. A mixture of lanthanum oxide with four-fifths its weight of sugar carbon is placed in a carbon tube closed at one end, and heated in the electric furnace with a current of 350 ampères and 50 volts. The product is *lanthanum carbide*, C_2La , which is distinctly crystalline, and is transparent and yellow in thin slices; sp. gr. = 5.02 at 20°. It is not attacked by fluorine at the ordinary temperature, but burns brilliantly in it when gently heated; it also burns in chlorine at 250°, and in bromine and iodine vapours at 255°. When heated to redness in oxygen, it burns completely, but remains practically unaffected by sulphur vapour at the softening point of glass, or by phosphorus vapour at 700—800°. Selenium vapour, on the other hand, converts the carbide into a selenide. Nitrogen at 700—800° has little effect on it, but the residue evolves small quantities of ammonia when fused with potassium hydroxide. Carbon dissolves in the fused carbide, but separates as well crystallised graphite on cooling. Fuming nitric acid has no action on the carbide, but concentrated sulphuric acid is reduced when heated with it; dilute acids decompose it readily. When heated in nitrous or nitric oxide, the carbide burns vigorously; it is also decomposed by hydrogen chloride below a dull red heat, and fused oxidising agents attack it readily.

When mixed with water, lanthanum carbide is rapidly decomposed at the ordinary temperature, with evolution of a gas which contains about 71 per cent. of acetylene, 1 to 2 per cent. of ethylene, and 27 to 28 per cent. of methane. Small quantities of liquid and solid hydrocarbons are formed at the same time. C. H. B.

Action of Mercury Salts on Aluminium. By PERCY A. E. RICHARDS (*Chem. News*, 1896, 74, 30—31).—Salts of mercury, or the metal itself, when brought into contact with aluminium, give rise to filamentitious excrescences of alumina, seemingly caused by the formation of an aluminium amalgam and its subsequent reaction with the moisture of the air. The excrescence reappears after washing and wiping, if the mercury has once obtained a firm hold. D. A. L.

Preparation of Potassium Permanganate by Electrochemical Means. By RICHARD LORENZ (*Zeits. anorg. Chem.*, 1896, 12, 393—395).—A solution of potassium permanganate can be prepared by passing a current of 1.5 volt potential between an anode of commercial manganese or of ferromanganese (containing 20—25 per cent. of iron) and a cathode of porous copper oxide (such as the positive plate of a "cupron-element"), these two electrodes dipping in a solution of caustic potash contained in a beaker. Ferric oxide collects at the bottom of the beaker. C. F. B.

Action of Halogen Compounds of Phosphorus on Iron, Nickel, and Cobalt. By A. GRANGER (*Compt. rend.*, 1896, 123, 176—178).—The author has investigated the action of the vapour of

phosphorus trichloride, tribromide, and diiodide on iron, nickel, and cobalt reduced from the oxide, or better, from the oxalate. At a red heat, iron and phosphorus trichloride yield the phosphide, Fe_4P_3 , in small, brilliant, iron-grey, prismatic crystals. Nickel, under the same conditions, yields the red, crystalline product described by Pelletier, but by prolonged action of the chloride, at a somewhat higher temperature, small, brilliant, yellowish-white crystals of the subphosphide, Ni_2P , are obtained. At a temperature above a red heat, but not exceeding bright redness, cobalt yields a subphosphide, Co_2P , which forms small, prismatic needles.

Phosphorus bromide does not readily attack the three metals under the conditions stated, and yields unsatisfactory results. The diiodide very readily yields the phosphides, Fe_4P_3 and Ni_2P , but does not readily attack cobalt. The trifluoride yields the same products mixed, however, with the corresponding fluorides and the products of the action of fluorine on glass.

The iron phosphide, Fe_4P_3 , is attacked with difficulty by aqua regia, but the nickel and cobalt subphosphides dissolve readily in it, and also in nitric acids. All three compounds are readily attacked by chlorine and by fused alkalis, and lose phosphorus when heated.

C. H. B.

Preparation of Potassium Dichromate by Electrochemical Means. By RICHARD LORENZ (*Zeits. anorg. Chem.*, 1896, 12, 396—397).—A solution of potassium dichromate can be prepared by passing a current of 2 volts potential between an anode of ferrochrome (containing about equal quantities of chromium and iron) and a cathode of porous copper oxide, the two electrodes dipping in a solution of caustic potash contained in a beaker. Ferric oxide collects at the bottom of the beaker.

C. F. B.

Combination of Iodic acid with other Acids. By PAUL CHRÉTIEN (*Compt. rend.*, 1896, 123, 178—180).—When 100 grams of sodium iodate and 70 grams of molybdic anhydride are boiled for some time with 3000—4000 c.c. of water, the salt,



is obtained in small, stellate groups of slender needles, slightly soluble in water, but soluble in nitric acid. The latter solution precipitates phosphoric acid in the form of a phosphomolybdate. Yellow molybdic acid, $\text{MoO}_3, 2\text{H}_2\text{O}$, is very soluble in hot sodium iodate solution, and the liquid deposits short needles, which, when dried at 100° , have the composition $\text{I}_2\text{O}_5, 4\text{MoO}_3, \text{Na}_2\text{O}$. Potassium iodate yields a salt, $\text{I}_2\text{O}_5, 2\text{MoO}_3, \text{K}_2\text{O}, \text{H}_2\text{O}$, which crystallises in brilliant lamellæ, and ammonium iodate yields an analogous compound. The corresponding barium salt crystallises with 2 mols. H_2O in a bulky mass of long, slender needles, and when a nitric acid solution of this salt is mixed with an equivalent quantity of sulphuric acid, a solution of *iodomolybdic acid*, $\text{I}_2\text{O}_5, 2\text{MoO}_3, 2\text{H}_2\text{O}$, is obtained; this crystallises when concentrated in a vacuum, but the acid is very soluble in water.

Freshly prepared tungstic acid is insoluble in solutions of iodates or of iodic acid, but metatungstic acid combines with iodic acid in

several proportions, and yields a series of iodotungstates when added to cold and somewhat dilute solutions of iodates. Potassium iodate yields crystals of the composition $2\text{I}_2\text{O}_5, 4\text{WO}_3, 2\text{K}_2\text{O}, 8\text{H}_2\text{O}$, analogous to the iodomolybdate.

When syrupy phosphoric acid is boiled with excess of iodic acid, brilliant, nacreous, prismatic crystals are obtained, which have the composition $\text{P}_2\text{O}_5, 18\text{I}_2\text{O}_5, 4\text{H}_2\text{O}$, and are rapidly decomposed by moist air, and converted into a white powder. C. H. B.

Action of Ammonia on Alkali Paratungstates. By L. A. HALLOPEAU (*Compt. rend.*, 1896, **123**, 180—182).—When a large excess of ammonia is added to a concentrated solution of potassium paratungstate, a crystalline precipitate is produced; this dissolves in hot water, from which it separates in crystals of the composition $12\text{WO}_3, 5\text{K}(\text{NH}_4)\text{O} + 11\text{H}_2\text{O}$. They are very thin, rhomboidal lamellæ, which act strongly on polarised light, show extinction at 27° from the axis of elongation, and generally resemble the prismatic crystals of the simple potassium or ammonium paratungstate. The double salt results from the combination in equal molecular proportions of the two simple salts, which are triclinic and isomorphous.

Under similar conditions, sodium paratungstate yields rhomboidal crystals of the compound $12\text{WO}_3, 4(\text{NH}_4)_2\text{O}, \text{Na}_2\text{O} + 14\text{H}_2\text{O}$, obtained by Gibbs by the action of ammonium phosphate on sodium paratungstate in presence of alcohol. If, however, ammonia is added drop by drop to a concentrated solution of the paratungstate until the precipitate redissolves with difficulty, the solution, when concentrated, yields crystals of the compound $12\text{WO}_3, 3(\text{NH}_4)_2\text{O}, 2\text{Na}_2\text{O} + 15\text{H}_2\text{O}$, already described by Marignac. It loses 12 mols. H_2O at 100° . The crystals are rhombic prisms, which act strongly on polarised light, and show extinction at 36° from the axis of elongation. The acid tungstate, $16\text{WO}_3, 3(\text{NH}_4)_2\text{O}, 3\text{Na}_2\text{O} + 22\text{H}_2\text{O}$, is also sometimes obtained from the same liquid in prismatic crystals which show extinction at 35° from the axis of elongation.

These results afford further evidence of the differences between the chemical properties of sodium and potassium paratungstates.

C. H. B.

Specific Gravity and Specific Heat of Alloys of Iron and Antimony. By J. B. VINCENT LABORDE (*Compt. rend.*, 1896, **123**, 227—228).—The alloys were prepared by fusing antimony and iron together in a brasqued crucible.

Iron per cent.	Sp. gr. at 0° .	Mean specific heat $0-100^\circ$.	
		Found.	Calculated.
18.48	7.211	0.0639	0.0625
25.69	7.912	0.0688	0.0670
35.42	8.300	0.0753	0.0731
39.20	8.071	0.0779	0.0754
43.12	8.298	0.0797	0.0778
55.02	8.159	0.0869	0.0854
61.20	8.120	0.0903	0.0892
81.20	7.800	0.1028	0.1019

The sp. gr. is always equal to or higher than that of iron, which is the heavier constituent, and hence the formation of the alloy is accompanied by considerable contraction. At first the sp. gr. increases rapidly with the proportion of iron, and afterwards diminishes but with less rapidity. The specific heat is always higher than the value calculated for a mixture, and the more important differences are much greater than the experimental error. An alloy containing 39.2 per cent. of iron, which corresponds somewhat closely with the formula Fe_3Sb_4 , shows the greatest divergence from the calculated specific heat, and its sp. gr. is also anomalous. Weiss has found that the magnetic properties of iron-antimony alloys increase suddenly when the proportion of iron reaches or exceeds that required by the formula Fe_3Sb_4 .
C. H. B.

Zirconates. By FRANK P. VENABLE and THOMAS CLARKE (*J. Amer. Chem. Soc.*, 1896, **18**, 434—444).—The best method for the preparation of the zirconates is to fuse gently dried zirconia with hydroxides, or, by prolonged heating of the oxides. In the case of the alkaline earths, zirconates are produced containing one equivalent of each oxide, such as CaO, ZrO . The lithium compound obtained was LiO, ZrO . In the case of the alkalis, it seemed to be possible to obtain zirconates having a largely preponderating proportion of zirconia.
J. F. T.

Reaction between Carbon Tetrachloride and the Oxides of Niobium and Tantalum. By MARC DELAFONTAINE and CHARLES E. LINEBARGER (*J. Amer. Chem. Soc.*, 1896, **18**, 532—536).—On passing the vapour of carbon tetrachloride over heated niobic pentoxide, contained in a hard glass tube, both the pentachloride and the oxychloride of niobium are formed, but the latter in by far the greater quantity; of the gaseous products of the reaction, phosgene seems to predominate; the yield of pentachloride is not increased by carrying out the experiment in an atmosphere of carbonic anhydride, or of chlorine, this again illustrating the great tendency of niobium to enter into combination as the niobyl group.

In the preparation of a large quantity of niobyl chloride, a small quantity of an orange-coloured sublimate, more volatile than the chloride, was formed; this the authors consider to be tungsten oxytetrachloride, its formation being due to the niobic acid used being slightly contaminated with a tungsten compound.

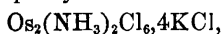
Carbon tetrachloride has no action on tantalic acid, even at a temperature high enough to cause Bohemian glass to soften.

J. F. T.

Action of Reducing Agents on Osmium Nitroso-compounds. By L. BRIZARD (*Compt. rend.*, 1896, **123**, 182—185).—The reduction of potassium osmiamate by formaldehyde in alkaline solution yields a black, gelatinous precipitate, which dissolves in hydrochloric acid, but does not crystallise, even in presence of alkali chlorides. It contains some nitrogen, but not in the form of ammoniacal nitrogen.

If a warmed solution of the osmiamate is mixed with a hydrochloric acid solution of stannous chloride, and the liquid is concen-

trated, after the addition of excess of potassium chloride, *potassium amidochlorosmiate*, $\text{NH}_2\cdot\text{OsCl}_3\cdot 2\text{KCl}$, is obtained in small, brilliant, maroon-brown crystals, which act strongly on polarised light. The analytical results agree equally well with the formula



but this is not admissible, because the salt is completely converted into the chlorosmiate, $\text{OsCl}_4\cdot 2\text{KCl}$, by strong hydrochloric acid.

The potassium amidochlorosmiate is soluble in water, but insoluble in common organic solvents. The greenish-yellow aqueous solution gradually becomes violet at the ordinary temperature, and deposits an amorphous precipitate of the same colour, but the stability of the solution is increased by the presence of hydrochloric acid or potassium chloride. The salt is only slightly soluble in a concentrated solution of potassium chloride, and this fact can be utilised in its preparation. When heated in air, it gives off hydrogen chloride, ammonium chloride, and osmium peroxide; when heated with aqueous potash, ammonia is evolved, and a violet-black precipitate is formed, which dissolves in hydrochloric acid, but will not crystallise. When evaporated with concentrated hydrochloric acid, the amidochlorosmiate yields a red, crystalline hydrochloride, $\text{NH}_2\cdot\text{OsCl}_3\cdot 2\text{KCl}\cdot\text{HCl}$, which, by further action of hydrochloric acid, is converted into the chlorosmiate, as already stated.

The amidochlorosmiate reduces permanganate, mercuric chloride, ammoniacal silver nitrate, cupric salts, and Fehling's solution.

C. H. B.

Mineralogical Chemistry.

The "Dilute Coloration" of Minerals. By ERNST WEINSCHENK (*Zeits. anorg. Chem.*, 1896, **12**, 375—392).—By dilute coloration is understood that colour of a mineral which is not natural to the pure substance, nor due to the presence of an isomorphous mineral, but is caused by the presence of a minute quantity of a coloured substance so distributed throughout the mass of the crystal that the resulting coloration exhibits the same relation to the symmetry of the crystal (pleochroism, &c.) as would a colour natural to the mineral itself. Such colorations were once attributed to the presence of "hydrocarbons," because they are destroyed, as a rule, by comparatively slight elevation of temperature. But this view is probably erroneous, for, although crystals of organic substances are readily dyed by organic colouring matters, this is rarely the case with inorganic crystals. Further, the author has demonstrated the presence of traces of titanium in smoky quartz from two different localities, whereas a specimen of colourless rock crystal was found to contain no titanium, even though in some parts of the crystal—not, of course, taken for analysis—crystals of rutile were imbedded. The smoky coloration cannot be due to titanate oxide, which is colourless, and it is suggested

that it is due to the deep-coloured sesquioxide, which becomes changed to the colourless oxide on ignition, so causing a loss of the coloration. It is further suggested that the analogous oxides of tin and zirconium likewise produce dilute coloration in minerals, and possibly also the oxides of cerium and of vanadium, and of metals related to these. Ferric oxide, too, is probably responsible for many "dilute" yellow and brown shades. In all cases, the colouring agent is to be regarded as of *inorganic* nature. As to the manner in which it is present, it may be regarded as in solid solution in the crystal, or, by those who reject the hypothesis of solid solutions, as existing in the interstices between the molecules of the mineral.

C. F. B.

Nitrogen and Argon in Fire-damp. By TH. SCHLÖSING, jun. (*Compt. rend.*, 1896, **123**, 233—236).—The proportion of nitrogen in fire-damp, collected in such a way as to avoid admixture with air, is very variable; in 20 specimens, the limits were 0.75 and 30.0 per cent. The proportion of argon in this nitrogen was 1.1 per cent., or almost exactly the same as in atmospheric nitrogen. Even in specimens of fire-damp issuing from the coal under high pressure, the percentage of argon in the nitrogen was 1.18. A large number of samples were analysed, and the results will be described subsequently; a considerable proportion of argon was found in every case.

Examination of the gases evolved from powdered coal in a vacuum indicates that argon, if present at all, does not occur in a higher proportion than 0.0005 per cent. by weight.

C. H. B.

Examination of Gases from certain Mineral Water. By ALEXANDER KELLAS and WILLIAM RAMSAY (*Proc. Roy. Soc.*, 1895, **59**, 68—69).—A sample of inflammable gas from "Allhusen's Well" was found to contain, besides the usual constituents, nitrogen, hydrocarbons, &c., 0.4 per cent. of indifferent gas, the spectrum of which corresponded with that of argon; the helium yellow lines were not visible.

An incombustible gas from another well at the same place was also found to contain 0.5 per cent. of argon. 660 c.c. of gas from a boiling spring near Reykjavik, Iceland, was found to contain 7.45 c.c. of argon, or 1.14 per cent. No helium could, however, be detected.

J. F. T.

An Attempt to determine the Condition in which Helium and the Associated Gases exist in Minerals. By WILLIAM AUGUSTUS TILDEN (*Proc. Roy. Soc.*, 1896, **59**, 218—224).—Experiments were made in order to find out whether the gas evolved from certain minerals by the application of heat was enclosed in cavities or existed in a state of so-called occlusion. Monazite, on being enclosed in a hard glass bulb and exhausted, was found to give off below 130° only carbonic anhydride and water vapour; from 130—140°, however, gas was evolved, which for the first time showed the D₃ line of helium; between this and 446° successive quantities of gas were evolved containing helium.

Cleveite was found to behave in a similar manner.

Experiments were then made for the purpose of ascertaining

whether the mineral from which the gas had been removed was capable of reabsorbing it. For this purpose, massive Swedish cleveite was employed, and it was found that the mineral did not reabsorb the helium mixture at the ordinary atmospheric pressure. In a second experiment, however, conducted under a pressure of $2\frac{1}{2}$ atmos., the mineral was found to have absorbed one-twenty-fifth of its volume of the gas. Further experiments were tried under greater pressure. The apparatus employed consisted of three glass bulbs, A, B, and C, connected by means of a horizontal glass tube, one end of which was attached to a Sprengel pump and the other to a movable reservoir of mercury capable of being raised to a great height. A contained cleveite which had been heated to 400° in a vacuum, B also contained cleveite heated to 170° in a vacuum, and C 7.5 grams of artificial lead uranate which had been heated to redness; the bulbs were heated to 100° and exhausted of air, the gas (prepared from cleveite and freed from carbonic anhydride and water) was then admitted at atmospheric pressure, and the horizontal tube at that end sealed off. The contents of the tubes were then subjected to a pressure of 7 atmos., and heated for 18 hours at 100° , the pressure being maintained for 96 hours. A was then found to have absorbed one-seventh of its volume and B more than one-fourth; the gas evolved from C consisted only of carbonic anhydride.

Cleveite, therefore, appears to reabsorb helium to an extent which is, roughly, proportional to the pressure.

As a result of further experiments, it was found that iron absorbs helium, but to a less extent than it does hydrogen, and palladium much less readily.

The gas evolved from red Peterhead granite was found to contain a large proportion of hydrogen, 15.2 grams of granite yielding 14.9 c.c. of gas, consisting of 24.8 per cent. of carbonic anhydride and 75.2 per cent. of hydrogen; no helium was evolved. Helium was not absorbed by the powdered mineral when treated in the same manner as cleveite.

J. F. T.

Japanese Coal. By FRANK BROWNE (*Chem. News*, 1896, **74**, 76—77).—The sample examined was Tubari coal from the island of Yezo. In lumps it is black, in powder chocolate-brown; it burns readily with a bright, smoky flame that soon subsides, leaving a glowing mass; it is non-caking, and contains, per cent., moisture, 3.83; volatile combustible matter, 36.62; fixed carbon, 42.70; ash, 16.85; the ultimate analysis showing C, 62.84; H, 6.37; N, 1.08; O (calculated), 11.01; S (combustible), 1.18; ash (containing 0.49 per cent. of sulphur), 17.52 per cent. Sp. gr. 1.411; heat of combustion calculated = 6,826 cal.

D. A. L.

Magnetic Behaviour of Pyrrhotite. By ANTAL ABT (*Zeits. Kryst. Min.*, 1896, **27**, 100—101; from *Értesítő az erd. Múzeum egyl. orv.-term.-tud. szakosztályából*, 1895, **17** (20th year), 20—30, and *Ger.*, 89—100).—The author has investigated the magnetic properties of those ores in which the metals are strongly paramagnetic, namely, ores of iron, nickel, cobalt, and manganese. Two specimens of

hæmatite, and all those of pyrrhotite, possessed magnetic polarity, whilst pyrites and nickel ores did not. Pyrrhotite shows a considerable amount of residual magnetism, exceeding that of magnetite, and its behaviour is similar to that of hard steel. The amount of iron in the ores examined is given by the analyses of G. Nyiredy as: magnetite, 68·20 and 67·50 per cent.; pyrrhotite, 57·58, 57·25, and 55·80 per cent. L. J. S.

Pyrrhotite from Borév. By MÓR PÁLFI (*Zeits. Kryst. Min.*, 1896, 27, 101; from *Értesítő az erd. Muzeum egyl. orv.-term.-tud szakosztályából*, 1895, 17 (20th year), 54—57).—Pyrrhotite occurs with pyrites and quartz at a limestone and phyllite contact near Borév (county of Torda-Aranyosér). The massive mineral is greyish-white with a tinge of red, and is somewhat impure owing to admixed silicate. Analysis gave:

Fe.	S.	Cu.	Insol.	Total.
57·78	35·34	trace	7·20	100·32

After deducting impurities, this is near to $\text{Fe}_{11}\text{S}_{12}$. Mean sp. gr. 4·497. L. J. S.

Some New South Wales and other Minerals. By ARCHIBALD LIVERSIDGE (*Chem. News*, 1896, 74, 113—116).—*Stibnite*, a hard, splintery variety with conchoidal fracture, from Queensland, gave, on analysis:

Sb.	S.	Fe.	SiO_2 .	BaSO_4 .	Total.	Sp. gr.
64·47	26·59	1·00	3·41	2·63	98·10	4·43

Silica and barytes occur as thin veins in the material.

Plumbiferous apatite occurs as crystals in cavities in zinciferous galena at Broken Hill. Probably part of the calcium phosphate is replaced isomorphously by lead phosphate; the crystals, however, enclose specks of galena. Pyromorphite has been found in the same mine.

Barklyite is found at Two Mile Flat, Mudgee, N.S.W., as small pebbles of a dull magenta colour. Hardness about 8·5; sp gr. 3·738. Tough, fracture granular; the powder is pale pink. It is a variety of corundum, which does not appear distinct enough to warrant a special name.

Chrysocolla is described from Broken Hill.

Beryl, from Vegetable Creek, New England, N.S.W., gave:

SiO_2 .	Al_2O_3 .	BeO .	Fe_2O_3 .	CaO .	Total.	Sp. gr.
67·4	18·5	12·9	0·6	trace	99·4	2·80

Crocoite, brilliant, deep orange-red crystals, from Dundas, Tasmania, gave:

PbO .	CrO_3 .	Fe_2O_3 .	Total.	Sp. gr.
66·86	30·99	1·02	98·87	5·92

Fahlerz, massive, from Wiseman's Creek, *via* Brewongle, N.S.W.

Cu.	Pb.	Fe.	Zn.	Sb.	S.	Ni, Co.	Total.
33·004	0·630	2·844	3·693	34·620	25·207	traces	99·998

This corresponds approximately to $\frac{4}{3}\text{CuS}\frac{1}{5}(\text{FeZn})\text{S}, \text{Sb}_2\text{S}_3$. Gold and silver are also present. [Note.—Tetrahedrite is $4\text{Cu}_2\text{S}, \text{Sb}_2\text{S}_3$.]

Ilmenite, from Cloncurry River, Queensland, gave :

TiO ₂ .	SiO ₂ .	FeO.	Fe ₂ O ₃ .	Total.
49·85	1·01	35·70	13·22	99·78

Manganese and magnesium are absent.

Zinciferous galena, occurring in nodules at Broken Hill, contains only a little zinc; blende is absent. The vein-stuff, however, gave :

Pb.	Zn.	S.	Fe.	Cu.	As, Sb.	Insol.	Total.
60·20	15·50	18·94	2·62	0·205	traces	3·16	100·625

This corresponds with $3\text{PbS} + 2\frac{1}{2}\text{ZnS}$, and seems to be related to huascolite and kilmacooite.

Limestone, from Picton, N.S.W., showing cone-in-cone structure, contained 68·20 per cent. CaCO_3 .

Molybdenite, from Eleanora mine, Kingsgate, near Glen Innes, N.S.W.; sp. gr. 4·6.

Mo.	S.	Fe.	Total.
57·31	42·00	1·50	100·81
58·66	41·23	0·39	100·28

Another specimen contained about 6 per cent. of manganese oxide, but probably mechanically enclosed between the folia.

Proustite is described from the United mine, Rivertree.

Scheelite, massive, from Lady Hopetoun mine, Glen Innes, N.S.W. Sp. gr. 5·93; of another portion, 5·3. It contains, besides CaWO_4 , a little water, 2·23 per cent. SiO_2 , 1·52 per cent. Fe_2O_3 , and a trace of manganese.

Cassiterite, from Elsmore mine, Inverell, N.S.W. I, stout pyramids; hardness 6·5; powder, white. II, water-worn fragments; hardness 7; powder, brown.

	SnO ₂ .	SiO ₂ .	Fe ₂ O ₃ .	MnO.	WO ₃ .	Total.	Sp. gr.
I.	94·60	2·00	1·67	0·25	0·06	98·58	6·68
II.	92·52	1·68	3·21	0·98	0·36	98·75	6·54

The loss in these analyses may indicate the presence of rare elements.

Topaz, in short prisms on granite, from the Shoalhaven district, gave the following mean of two analyses :

SiO ₂ .	Al ₂ O ₃ .	F.	H ₂ O (at 100°).	Total.	Sp. gr.
28·19	62·66	14·01	1·21	106·07	3·56

L. J. S.

Pearceite, and the Crystallisation of Polybasite. By SAMUEL L. PENFIELD (*Amer. J. Sci.*, 1896, [4], 2, 17—29; and *Zeits. Kryst. Min.*, 1896, 27, 65—77).—As corresponding sulpharsenites and

sulphantimonites usually receive different designations, the name pearceite, after Richard Pearce, is proposed for the arsenical varieties of polybasite, $9\text{Ag}_2\text{S}, \text{Sb}_2\text{S}_3$, pearceite being $9\text{Ag}_2\text{S}, \text{As}_2\text{S}_3$. Minerals to which this name can be applied are the arsenical polybasite from Schemnitz analysed by H. Rose, in 1833; that of Aspen, Colorado, described by Penfield; by S. H. Pearce (Abstr., 1893, ii, 75); and the mineral described in the present paper. Two other old analyses show arsenic and antimony in about equal molecular proportions.

The mineral here described occurs beautifully crystallised at the Drumlummon mine, Marysville, Lewis and Clarke Co., Montana. Analysis by F. C. Knight gave the following results:

S.	As.	Ag.	Cu.	Fe.	Insol.	Total.
17.71	7.39	55.17	18.11	1.05	0.42	99.85

This gives S : As : ($\text{Ag}_2 + \text{Cu}_2 + \text{Fe}$) as very nearly 12 : 2 : 9, as is required by the above formula, with $\text{Ag}_2 : \text{Cu}_2 : \text{Fe} = 255 : 143 : 19$. The monosymmetric crystals are usually flat, hexagonal tablets, often with highly modified edges. $a : b : c = 1.7309 : 1 : 1.6199$; $\beta = 89^\circ 51'$; $mm = 60^\circ 2'$. On the basal plane are triangular markings, and the crystals show indications of twinning. The colour and streak are black; lustre, metallic; opaque, even in thin splinters. Sp. gr. 6.15. Brittle with no distinct cleavage.

Polybasite, which has been described as being rhombohedral, and more recently as orthorhombic, is here shown to be monosymmetric. A crystal from Himmelfahrt mine, Freiberg, is described, which consists of a rhombohedron with basal plane; this would be difficult to explain if the mineral were orthorhombic. Measurements of perfect crystals from Yankee Boy mine, Ouray, Colorado, gave $a : b : c = 1.7309 : 1 : 1.5796$; $\beta = 90^\circ 0'$; $mm = 60^\circ 2'$.

These parameters of pearceite and polybasite show that there is a tendency for arsenic to increase the length of the vertical axis, and this is also to be noticed in several other cases, for example, in proustite and pyrrargyrite. A close similarity is pointed out between these parameters and those of copper glance (Cu_2S), stromeyerite (CuAgS), and many sulpharsenites and sulphantimonites, all of which have a prism angle of nearly 60° ; this would seem to indicate that the sulphide of the metal has had a controlling influence on the crystallisation.

L. J. S.

Rathite, a new Binnenthal Mineral. By HEINRICH BAUMHAUER (*Zeits. Kryst. Min.*, 1896, 26, 593—602).—Rathite is very similar in appearance to the Binnenthal minerals, jordanite, dufrenoyite, and sartorite, which are also compounds of lead, arsenic and sulphur; it is distinguished from these by the presence of parallel systems of very fine striæ, by the twinning, and by the crystal angles. The fine striæ are seen with the aid of a lens, in light at a particular angle, on the crystal faces and on fractured surfaces; it is evidently due to a lamellar structure (which may be isomorphous banding or twinning) of the crystals parallel to the faces of a brachydome. The crystals are orthorhombic, and, like those of the minerals mentioned above,

are elongated and striated in the direction of the macroaxis, and are rich in macrodomes. In the twin crystals, the striated zones of two individuals intersect at an acute angle.

$$a : b : c = 0.668099 : 1 : 1.057891.$$

Multiplying a and c by $\frac{3}{2}$, there is a close relationship between these parameters and those of dufrenoyite. Sp. gr. 5.32. Analysis by A. Bömer gave:

Pb.	S.	As.	Sb.	Fe.	Total.
52.98	23.72	17.24	4.53	0.56	99.03

The antimony is probably too low. A mixture of 5 mols. of dufrenoyite ($2\text{PbS}, \text{As}_2\text{S}_3$), and 1 of jamesonite ($2\text{PbS}, \text{Sb}_2\text{S}_3$), does not correspond so closely to this composition as does a mixture of 5 mols. of $2\text{PbS}, \text{As}_2\text{S}_3 + 2\text{PbS}, \text{As}_2\text{S}_3 = 4(\text{PbAsS}_3)$, and 1 of $2\text{PbS}, \text{Sb}_2\text{S}_3 + 2\text{PbS}, \text{Sb}_2\text{S}_3 = 4(\text{PbSbS}_3)$; the second formula is adopted, and is also expressed structurally. It is supposed that the fine striæ are due to the alternate banding of these two isomorphous compounds, and that the partial replacement of As_2S_3 and Sb_2S_3 by As_2S_5 and Sb_2S_5 accounts for the morphotropic relationship between rathite and dufrenoyite. The mineral is named after the late G. vom Rath.

L. J. S.

[**Calcistrontite, "Feather Ore," &c.**] By E. A. HUGO LASPEYRES and E. KAISER (*Zeits. Kryst. Min.*, 1896, **27**, 41—59).—Calcistrontite was the name used by von der Marck (*Verh. Ver. Rheinlande und Westfalens*, 1882, **39**, 84, Corr.-bl.) for a mineral from Drensteinfurt, near Hamm, Westphalia, which he considered to be an isomorphous mixture having the composition $3\text{CaCO}_3, 2\text{SrCO}_3$. It is here shown to be a mixture of calcite and strontianite; grains of granular strontianite being enclosed in crystalline calcite, the calcite itself forming a granular aggregate. This is well seen in microscopic sections, and, by means of heavy solutions, the two minerals can be separated.

By means of microchemical tests, and the indications of cleavage, it is shown that what has been labelled as "feather ore," from various localities, is really capillary stibnite, and not jamesonite.

A simple apparatus for use in separating minerals by means of heavy solutions is described.

Crystallographic and other notes are given concerning copper glance, blende, quartz, &c.

L. J. S.

Pollucite, Manganocolumbite and Microlite from Rumford, Maine. By H. W. FOOTE (*Amer. J. Sci.*, 1896, [4], **1**, 457—461; and *Zeits. Kryst. Min.*, 1896, **27**, 60—64).—These minerals occur at Black Mountain, Rumford, Maine, in a coarse pegmatite, together with quartz, albite, muscovite, tourmaline, lepidolite, spodumene, amblygonite, beryl, cassiterite, and columbite. The pollucite occurs in irregular masses, and closely resembles white quartz in appearance, but some small particles are colourless and transparent. The material separated for analysis had sp. gr. 3.029—2.938; the cæsium

was separated and estimated as Cs_2PbCl_6 ; only a trace of rubidium was detected by the spectroscope. The mean of two analyses is:

SiO_2 .	Al_2O_3 .	Cs_2O .	K_2O .	Na_2O .	Li_2O .	H_2O .	Total.
43.64	16.84	36.14	0.37	2.09	0.08	1.58	100.74

This gives the same formula as that recently deduced by Wells for the mineral from Hebron, namely, $\text{H}_2\text{Cs}_4\text{Al}_4(\text{SiO}_3)_9$.

The dark, reddish-brown manganocolumbite is described crystallographically; $a:b:c = 0.8359:1:0.8817$. Sp. gr. 6.44. The honey-yellow, octahedral crystals of microlite have sp. gr. 5.17.

L. J. S.

Mineralogical Notes [Scapolite, &c.]. By ALFRED J. MOSES (*Zeits. Kryst. Min.*, 1896, **26**, 603; from *School of Mines Quart.*, 1894, **14**, 323).—The ettringite described by the author from Tombstone, Arizona (Abstr., 1893, ii, 536) incrusts, and has evidently been derived from, a silicate which the following analyses show to be an altered scapolite. It is white (Anal. I) or pale green (II), incoherent and corroded, and mixed with ores.

	SiO_2 .	Al_2O_3 .	CaO .	MgO .	Na_2O .	H_2O (at 110°).	H_2O (ignition).
I.	45.86	21.56	12.79	2.43	1.16	4.45	11.74
II.	45.50	21.14	11.96	1.34	—	7.07	12.98

Impurities have been deducted and the analyses calculated to 100. Formula, $(\text{SiO}_4)_{15}\text{Al}_8(\text{Ca}, \text{Mg}, \text{Na}_2)_6\text{H}_{24} + 6\text{H}_2\text{O}$. Sp. gr. 2.66. The gigantic crystals of gypsum from near South Wash, Wayne Co., Utah, are described; also heulandite and stilbite from New Jersey.

L. J. S.

Physiological Chemistry.

Gaseous Exchanges in Inhabitants of the Tropics. By C EIJKMAN (*Pflüger's Archiv*, 1896, **64**, 57—78).—The oxygen used up was found to be, for Europeans in Europe 250·3, in India 245·7, and for Malaysians, 251·5 c.c. per minute. The respiratory quotient for the same three classes is 0·775, 0·768, and 0·856 respectively. The differences are thus but small, and give little information as to the influence of climate on heat-regulation. The high respiratory quotient in the case of the Malaysians follows from their richly carbohydrate diet.
W. D. H.

Percentage of Argon in Atmospheric and Respired Air. By ALEXANDER KELLAS (*Proc. Roy. Soc.*, 1895, **59**, 66—69).—Experiments were made on the comparative amount of argon in ordinary air, and in air which had been frequently breathed, with the view of ascertaining whether, if the proportion of oxygen and carbonic anhydride in air be very much altered, argon would enter into, or be expelled from the respiratory system.

The amount of argon in 100 c.c. of atmospheric nitrogen was found

to be 1.186 c.c., which owing to the avoidance of the presence of water, is probably more accurate than the numbers 1.04, 1.03, and 1.11 c.c., originally found by Lord Rayleigh and Ramsay.

One hundred c.c. of nitrogen and argon of breathed air (of normal composition) were found to contain 1.210 c.c. of argon.

The percentage is larger than in normal air, but the difference is not great; it would appear, therefore, that argon, like free nitrogen, plays no important part in the animal economy, save as a diluent.

J. F. T.

Action of Pancreatic Juice on Milk. By WILLIAM D. HALLIBURTON and T. GREGOR BRODIE (*J. Physiol.*, 1896, **20**, 97—106).—Doubt having arisen as to whether the results obtained with extracts of the pancreas are applicable to those obtained with the secretion of that organ, the present experiments were performed with the pancreatic juice obtained from dogs by means of a temporary fistula.

The action which the juice has on milk is different from that of rennet, a precipitate of casein occurring in the warm bath (at 35°—40°) in a finely granular form, the milk to the naked eye undergoing no change in its fluidity. On cooling this to the temperature of the air, it sets to a coherent curd which contracts to only a small extent, and is again broken up into fine granules by warming to 35°, the milk apparently becoming fluid again. This may be repeated a great number of times. This phenomenon is not prevented, but only slightly hindered by such an addition of potassium oxalate as completely inhibits the activity of rennet. Experiments performed with extracts of the gland lead to similar results, which may be masked if the action of the tryptic ferment is very energetic. The precipitate produced may be provisionally termed "pancreatic casein." By the action of rennet, it is converted into true casein. Its solubilities are partly like those of caseinogen, partly like those of casein. It is probably something intermediate between the two.

W. D. H.

Metabolism in Poisoning by Carbonic Oxide and Nitrobenzene. By EGMUND MÜNZER and P. PALMA (*Chem. Centr.*, 1896, i, 55—56; from *Zeits. f. Heilk.*, **15**).—In carbonic oxide poisoning there is an increased katabolism in the body. A larger amount of nitrogen than usual leaves the body as ammonia and uric acid, and the excretion of acetone is also increased; this diminishes the next day. The excretion of phosphoric acid is normal for the first two days, and sinks below the normal during the third and fourth day. Glycosuria may occur, and lactic acid be present in the urine, as Araki pointed out.

In a case of poisoning by nitrobenzene, the nitrogen excreted was small, the amount of phosphoric acid was about the normal, and ethereal hydrogen sulphates were increased. On the fourth day glycosuria made its appearance. Poisoning by these substances is compared to that by phosphorus.

W. D. H.

Use of Sugar in Cattle Feeding. By MALPEAUX (*Ann. Agron.*, 1896, **22**, 231—296).—Two heifers and two bullocks of known weight were fed with clover hay (2 kilos.), oat straw (5 kilos.),

maize and cotton cake, in addition to pasture. For 25 days one of each received besides, 500 grams of sugar daily. The results of the experiments were not very decisive, but sugar seemed to assist production of meat, being both a maintenance and a fattening food.

In experiments with cows, sugar did not increase milk production, or appreciably affect the composition of the milk. N. H. J. M.

Nutritive Value of Casein. By GOTTHELF MARCUSE (*Pflüger's Archiv*, 1896, **64**, 223—248).—The experiments were conducted in the usual manner of experiments on metabolism and full details are given. The main conclusion is that the nutritive value of casein is the same as that of the proteids of flesh. W. D. H.

Intestinal Absorption. By E. WAYMOUTH REID (*J. Physiol.*, 1896, **20**, 298—309).—The general conclusion drawn from the experiments described, is that the effects of excitation and section of the mesenteric nerves on the absorption of peptone and water, can be explained by the concomitant changes in the blood supply to the loops of gut induced by the action of the vaso-motor nerves on the arterioles, and there is no proof of the existence of specific absorptive nerve fibres. W. D. H.

The Basophil Constituent of Sympathetic Nerve-cells. By F. C. EVE (*J. Physiol.*, 1896, **20**, 334—353).—The granules in nerve-cells that have an affinity for basic dyes like methylene-blue have been long known, and some observers have described in them changes as the result of activity. In the present research, this basophil constituent was investigated in sympathetic nerve-cells, and the only change to be detected in them as the result of protracted activity is a slight diffuse blue stain in the cell substance, which is attributed to the formation of acid by the cell, and a consequent slight solution and diffusion of the basophil material. W. D. H.

Physiology of the Embryonic Heart. By JOHN W. PICKERING (*J. Physiol.*, 1896, **20**, 165—222; compare Abstr., 1893, ii, 424).—The hearts of mammalian embryos, even after being excised from the mother, maintain a fairly constant individual rhythm for three or four days, if they are bathed in a suitable nutrient material. The best nutrient was found to be a mixture of equal parts of the mother's blood, and 0.75 per cent. solution of sodium chloride. If the mother's blood is replaced by that of another species, or by egg-albumin, the beating of the heart becomes irregular, although it may last for several days. The sodium chloride solution alone will maintain activity for one day; the sustaining power of Ringer's solution, the ash of blood, and of gum arabic is about the same as that of sodium chloride. Grimaux's "colloïde aspartique" is nearly as good as blood; the "colloïde amidobenzoïque" kills in from 18 to 24 hours. Water, distilled in glass receivers, is innocuous, although not sustaining; water distilled in metal receivers is toxic (oligo-dynamic action). The general results with drugs are similar to those previously obtained with chick embryos, except that muscarine nitrate and atropine sulphate

exhibit their typical and antagonistic action on both early and late embryos. This, however, is not the case, in the chick's heart prior to the development of a nervous mechanism; chloroform is a depressant, but a small quantity of alcohol mitigates this action. Ether, except in large doses, applied direct to the heart is a stimulant. A large section of the paper is devoted to the action of electrical currents on the heart. W. D. H.

Estimation of Ethylic Alcohol in the Blood after introduction of the Liquid into the Veins, or the Vapour into the Lungs. By NESTOR GRÉHANT (*Compt. rend.*, 1896, 123, 192—194).—Alcohol of 25 per cent. was injected into the jugular vein of a dog until the quantity of alcohol was about $1/25$ th of the weight of the blood, which approximates to a toxic dose. The quantity of alcohol present was determined at intervals by means of a modification of the dichromate process. In one case in which the quantity of alcohol injected was 4.9 c.c. in 100 c.c. of blood, there was only 0.72 c.c. after half an hour, 0.54 c.c. after $1\frac{1}{2}$ hours, 0.45 c.c. after $2\frac{1}{2}$ hours, and 0.15 c.c. after $17\frac{1}{2}$ hours. The alcohol passes into the lymph, or is absorbed by the tissues. In another case only 0.2 c.c. of alcohol remained in 100 c.c. of blood after 15 hours, and it had all disappeared after $23\frac{1}{2}$ hours.

When a dog was made to inspire air saturated with alcohol vapour at 22° , 100 c.c. of blood contained 0.1 c.c. of alcohol after two hours' respiration, 0.31 c.c. after four hours, and 0.50 c.c. after six hours. At this point the experiment was stopped; the animal was very ill, but it recovered during the night. C. H. B.

Blood Coagulation in Albinos. By JOHN W. PICKERING (*J. Physiol.*, 1896, 20, 310—315).—The condition of the blood varies in animals that are sometimes in an albino and, at other times, pigmented condition. During the albino condition of the Arctic hare, intravenous injection of a nucleo-proteid or of Grimaux's synthesised proteid-like colloids fails to produce intravascular coagulation, whilst during the pigmented condition, coagulation is produced. When the animal is in a transition stage, the effects are inconstant. The "colloïdes amido-benzoïques" of Grimaux are without effect on extravascular blood (dogs and rabbits), but the addition of "colloïde aspartique" to the blood immediately it is shed, hastens its coagulation. W. D. H.

Initial Rate of Osmosis of Blood Serum. By W. S. LAZARUS-BARLOW (*J. Physiol.*, 1896, 20, 145—157; compare this vol., ii, 196).—At a temperature of 37° , the blood serum of the ox, horse, and sheep is in osmotic equilibrium with a 1.6 per cent. solution of sodium chloride placed on the other side of the membrane. This is approximately the same as saying that the initial rate of osmosis of the serum is equal to that of a 1.6 per cent. solution of sodium chloride. The greater the amount of proteid which a specimen of serum contains, the more concentrated must be the solution of sodium chloride on the other side of the membrane to produce osmotic equilibrium. Owing to dialysis, a solution of sodium chloride which at first in-

creases in quantity at the expense of the serum, may, later, become absorbed by the serum. W. D. H.

Sugar-formation in Alcohol Coagulated Liver. By FREDERICK W. PAVY (*Proc. Physiol. Soc.*, 1896, 4—6).—That sugar rapidly appears in the liver after death is an established fact. It is maintained that this is strictly a *post-mortem* phenomenon, and not a true picture of what occurs during life. It is a ferment action, not a vital action, and occurs equally well in a liver which has been coagulated by alcohol immediately after its removal from the body, and then kept in alcohol for months; on being dried and exposed to a suitable temperature in water, sugar is formed in amount approximately equal to that obtained from the fresh liver. W. D. H.

Behaviour of Polysaccharides with certain Animal Secretions and Organs. By EMIL FISCHER and W. NIEBEL (*Chem. Centr.*, 1896, i, 499—501; from *Sitzungsber. kgl. pr. Akad. Wiss.*, 1896).—Fluids like blood serum, or clear solutions or infusions of various organs were used, toluene or sodium fluoride being added to prevent the activity of living cells; the carbohydrate was added, and the mixture kept in a warm bath for 24 hours. Acetic acid was then added, the mixture boiled, the proteid filtered off, and the filtrate examined for carbohydrates. The results obtained were the following:—Starch, glycogen, and maltose are changed into dextrose by the secretions of different animals. Lactose is not affected by blood-serum; extracts of portions of the small intestine, especially in young animals, however, affect its hydrolysis; it is not affected by any other secretion. Cane-sugar is not affected by blood, or by infusion of stomach; extracts of duodenum of ox and sheep differ from those of other animals by also giving a negative result. Trehalose is feebly hydrolysed by the same extract from some animals, and not at all by that from others. Blood-serum is also ineffective, except that obtained from certain fishes—especially the carp. Raffinose is not altered by the invertin of the intestine, which must, therefore, be a different substance from the invertin of yeast.

Certain glucosides were also investigated. α -Methylglucoside, although so readily decomposed by beer yeast, is unaffected, or only slightly affected, by animal secretions and extracts; β -methylglucoside was decomposed by the secretion of the horse's small intestine. Amygdalin was readily decomposed by the contents of the rabbit's small intestine, but hardly at all by that of the dog. Throughout the experiments great differences are observable—according to the animals used. W. D. H.

Separation of Colloïds and Crystalloïds. By CHARLES J. MARTIN (*J. Physiol.*, 1896, 20, 364—371).—The filtering apparatus described briefly consists of a Pasteur filter, in the pores of which a membrane of gelatin or silicic acid has been deposited; the filtration being effected under pressure; colloïd substances do not, crystalloïd substances do, pass through the filter. The native proteïds (albumins, globulins, caseinogen, and nucleo-proteïds), glycogen, soluble starch, hæmoglobin, hæmatin, and the lipochrome of serum and egg-

white do not pass the filter. Alkali albumin and acid albumin pass through to a slight degree. Caramel, biliverdin, and dextrins pass through partially. Proteoses, urochrome, and crystalloids pass through. The crystalloids pass through at the same rate as water. The colloïd substances which are in true solution do not pass the membrane on account of the large size of their molecules. That albumin is in true solution is evident from the fact that it exerts osmotic pressure.

The membranes are recommended for use in the study of diffusion, undisturbed by mixing caused by convection currents, but more particularly for the effective separation of crystalloids from colloids, which is much required in the manipulations of chemical physiology.

W. D. H.

Influence of Food containing Nucleïn on the Formation of Uric acid. By F. UMBER (*Chem. Centr.*, 1896, 617; from *Zeit. Klin. Med.*, 29, 174—189).—The administration of a large amount (500 grams *per diem*) of food like thymus, which contains a considerable quantity of nucleïn, increases the excretion of uric acid, as compared with that passed when a similar amount of flesh is given. The same amount of liver in one person caused an effect similar to that caused by thymus, but in others its action was less marked. Kidney and brain gave nearly the same amount of uric acid as flesh, and milk less still. The xanthine bases are increased by administration of alkalis, and of milk.

W. D. H.

Influence of Atropine on the Secretion of Urine. By LUDWIG WALTI (*Chem. Centr.*, 1896, i, 263; from *Arch. exp. Path. Pharm.*, 36, 411—436).—Atropine lessens the secretion of urine, and hinders the action of diuretics. The injection of large or small quantities of urea into the circulation leads to glycosuria. Simultaneous injection of atropine prevents this.

W. D. H.

Creatinine. By PERCY COOPER COLLS (*J. Physiol.*, 1896, 20, 107—111).—Urinary creatinine, like sugar, is precipitated from aqueous solutions and from urine, when Brücke's lead-acetate method is employed. It is probable that Pavy's high figure for the percentage of sugar in normal urine is due to this circumstance.

Blood contains a small but ponderable amount of creatinine; in sheep's blood the percentage found being 0.000095. Creatinine was separated from the blood as the spherical mercury salt by a slight modification of G. S. Johnson's process.

W. D. H.

A New Solvent for Urinary Pigments. By WILLIAM KRAMM (*Chem. Centr.*, 1896, i, 713—715; from *Deutsch. Med. Woch.*, 22, 25—27, 42—45).—Liquid phenol is a direct solvent of the urinary pigments. Twenty parts of urine are shaken with one of phenol, the urine having first been saturated with a neutral salt, such as sodium chloride or sulphate, or ammonium sulphate; the pigments then pass into the phenol. Tricresol behaves in the same way, but more slowly. The phenol extract is mixed with ether and shaken with water; the water becomes yellow, the phenol and ether reddish. The

yellow pigment is urochrome, the reddish one urobilin. The red pigment of urate deposits is not soluble in phenol. W. D. H.

Phloridzin Diabetes. By NATHAN ZUNTZ (*Chem. Centr.*, 1896, i, 613; from *Du Bois Reymond's Archiv.*, 1895, 570—574).—An important difference between ordinary diabetes and that produced by phloridzin, is that in the former case the blood is rich in sugar, in the latter it is not. The kidneys must, therefore, in this case act most energetically in withdrawing the sugar from the blood. This increase in the power of the kidney cells was proved by an experiment on a dog in which the urine was collected separately from the two kidneys, into the renal artery of one of which a small amount of phloridzin solution was injected; this one secreted urine containing sugar, the other secreted normal urine. W. D. H.

Alloxuric Substances in the Urine in Nephritis. By G. ZÜLZER (*Chem. Centr.*, 1896, i, 616—617; from *Berlin Klin. Woch.*, 33, 72—75).—In health, according to Kolisch, nuclein derivatives are mainly transformed in the kidneys into the non-toxic uric acid, while a small part passes out as the poisonous alloxuric bases. The normal amount of these bases *per diem* is given as 0.04—0.06 gram, and the relation between their nitrogen and that of uric acid as 1 : 3.82; or the nitrogen of alloxuric bases, to that of total alloxuric substances as 1 : 4.82. His expectation that this relationship would be upset in nephritis is, in the present research, not confirmed.

W. D. H.

Febrile Albumosuria. By LUDOLF KREHL and MAX MATTHES (*Chem. Centr.*, 1896, i, 54—55; from *Deutsch. Arch. Klin. Med.*, 54, 501—514; and *Chem. Centr.*, 1896, i, 263; from *Arch. exp. Path. u. Pharm.*, 36, 437—450).—Many proteid substances raise the body temperature, and appear partly in a hydrated form in the urine. The elevated temperature in many acute specific fevers can be partly accounted for in this way, and proteoses are found in the urine. Deuteroproteose is the form most frequently found, and is believed to originate from the bacterial decomposition of nucleo-proteid.

Tuberculous animals respond especially well, by a febrile reaction, to small injections of proteose. Toxic proteids, like ricin, abrin, and tuberculin produce similar results.

W. D. H.

Effect of Drugs on the Tracheal Secretion. By JAMES CALVERT (*J. Physiol.*, 1896, 20, 158—164).—A window in the trachea of an animal (cat under chloroform, urethane, or morphine) being made, and the surface dried by blotting paper, drugs were injected into a vein or subcutaneously, and the rate of formation of secretion observed, and compared with that before the administration of the drug. It was found that alkalis increase the secretion in spite of Rossbach's assertion (*Berlin klin. Woch.*, 1882) to the contrary; that potassium iodide acts similarly, and emetine only markedly so. Saponin (senegin) in small doses does not increase secretion; in

large doses it diminishes it. Cold and heat applied to the abdomen increase and diminish secretion respectively. W. D. H.

Toxicological Notes on Ortho- and Para-Compounds.
THOMAS BOKORNY (*Pflüger's Archiv*, 1896, **64**, 306—312).—Experiments are described which show that in the same organism para-compounds are more poisonous than the corresponding ortho-compounds. W. D. H.

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Chemistry of Vegetable Physiology and Agriculture.

Influence of Oxygen on Yeast Fermentation. By R. RAPP (*Ber.*, 1896, **29**, 1983—1985).—The author has repeated the experiments of Chudiakow (*Abstr.*, 1895, ii, 282) on the influence of oxygen and hydrogen on the fermentation produced by yeast, and finds that, contrary to Chudiakow's statement, oxygen does not exercise any retarding effect. The passage of a rapid stream of either gas does produce a diminution of the fermentation, and the author suggests that in the former experiments the oxygen may have been passed more rapidly through the mixture than the hydrogen, and thus have produced a relative diminution of the action of the yeast.

A. H.

Fermentation of Uric acid by Micro-organisms. By ERNEST GÉRARD (*Compt. rend.*, 1896, **123**, 185—187).—The author has previously shown (*Compt. rend.*, **122**, 1019) that uric acid dissolved in sodium phosphate solution is converted into urea and ammonium carbonate by the action of micro-organisms derived from the air, and has suggested that the ammonium carbonate results from the action of some urophagic microbe on the urea, the latter being the true product of the fermentation of the uric acid.

Cultivations in peptonised broth have not led to the isolation of the bacilli or cocci which act on the uric acid, but they have enabled the author to separate these organisms from those which convert urea into ammonium carbonate. When mixed with selected cultivations, the uric acid, dissolved in sodium phosphate solution, is completely converted into urea, but the latter remains unchanged even after several months. Magnier de la Source has shown that when uric acid is boiled with water, it is converted into dialuric acid, and that the latter, when hydrolysed, yields urea and tartronic acid. The author considers that the chemical action of the micro-organisms on uric acid is represented by the equation $C_5H_4N_4O_3 + 4H_2O = 2CON_2H_4 + C_3H_4O_5$.

C. H. B.

Nitrification. By EMIL GODLEWSKI (*Ann. Agron.*, 1896, **22**, 303—304; from *Anzeiger Akad. Wiss., Krakau*, 1895, 178—192).—The results of previous experiments (*Abstr.*, 1893, ii, 544) indicated that nitrifying organisms probably derive their carbon from carbonic an-

hydride, and not from carbonates. Three experiments are now described, in which the same amounts of solutions of ammonium sulphate (with magnesium carbonate) were inoculated at the same time with pure cultivations of nitrifying organisms. In two experiments the apparatus was filled with air containing carbonic anhydride, in the third with pure air. At the end of the experiments, the air was measured and analysed. With carbonic anhydride, there was a reduction of volume, whilst with air alone there was no reduction. Magnesium carbonate was not available as a source of carbon, but, in presence of carbonic anhydride, nearly the whole of the ammonia was converted into nitrous acid. A portion of the nitrogen of the ammonia is liberated. The amount of free nitrogen produced varies according to the conditions of the experiment. N. H. J. M.

Nitrification. By MARCILLE (*Ann. Agron.*, 1896, **22**, 337—344).—Experiments were made on the relative suitability of ammonium sulphate and phosphate for nitrification. Whilst the phosphate was not found to be more suitable for the production of nitrous acid, it seemed more favourable than the sulphate in transforming nitrous into nitric acid.

As regards the rate of nitrification in different soils, it was found that in a given time a soil from Guadeloupe produced far more nitrates than a soil from Eure-et-Loir. This could not be due to the greater energy of the nitrifying organisms in the Guadeloupe soil, since the addition of a few grams of this soil to the French soil had no effect. It is concluded that the energy with which a soil is nitrified depends not only on the temperature, aëration, and humidity of the soil, and on the energy of the organisms present, but also on the nature of the organic matter to be nitrified. N. H. J. M.

Comparative Studies on the Poisonous Action of various Chemical Substances on Algæ and Infusoria. By THOMAS BOKORNY (*Pflüger's Archiv*, 1896, **64**, 262—306).—A very exhaustive paper; the experiments were performed on types of lower animal and vegetable life, and the strength of the poison noted which produced pathological changes or death. In this way, inorganic acids and bases, numerous salts, various oxidising agents (among which free halogens and potassium permanganate were the most toxic), phosphorus, organic acids, hydrocarbons, alcohols, halogen compounds, aldehydes, nitro-derivatives, sulpho-derivatives, cyanogen compounds, amido-compounds, alkaloids, and poisonous proteïds (abrin and ricin, which are only slightly poisonous to lower organisms) were investigated. W. D. H.

Digestion of Cellulose by Enzymes. By J. GRÜSS (*Chem. Centr.*, 1896, i, 313; from *J. Landw.*, **43**, 379—458).—Previous observers have described the solution of vegetable cell-walls by ferments during germination; this action is ascribed in malt extract to a special ferment (cytase). It is found that the hemicelluloses

undergo hydrolytic decomposition easily, although various members of the group show differences in this respect. W. D. H.

Decomposition of Vegetable Matters. By EMILE BRÉAL (*Ann. Agron.*, 1896, **22**, 362—375).—When water is kept in contact with dead vegetable matter, organisms develop which attack the organic matter, producing ammonia until the liquid becomes too alkaline. When, however, soil, containing nitrifying organisms, is added, the production of ammonia continues, as that already formed is converted into nitrates. If a vegetable infusion is poured on to a lump of soil, the ammonia produced disappears at the surface of the soil, where it is converted into nitrates, but inside the lump of soil there is an accumulation of ammonia, owing to want of aëration; even the nitrates originally present in the interior of the soil are reduced.

Humus becomes soluble in vegetable infusions owing to the ammonia which is liberated, but ceases to be dissolved when soil, containing nitrifying organisms, is added.

Vegetable infusions which have become too alkaline (ammoniacal) to support the life of ammonia-producing organisms, develop moulds which re-absorb the ammonia, producing new nitrogenous substances. This is what takes place on meadows and on peat where nitrifying organisms are absent. N. H. J. M.

Assimilation of the Nutritive Matter of the Soil by Rye. Manurial Requirements of Rye. By REMY (*Ann. Agron.*, 1896, **22**, 344—346; from *J. Landw.*, 1896, **44**, 31—103).—Experiments were made on the effect of various manures (nitrogenous, potash, and phosphatic) on the morphological development of rye. In 1891, nitrogen was taken up in proportion to the production of dry matter during the spring; whilst, in 1893, the nitrogen assimilated was in excess during this period, and the assimilation of nitrogen ceased in this year at the time when, in 1891, it had reached its greatest intensity. This is attributed to the dry season in 1893. Analogous results were obtained in 1881 by Dehérain and Meyer (*Abstr.*, 1883, 493).

As regards the relation between assimilation of potash and phosphates, and production of dry matter, the climatic conditions do not seem to have the same influence as in the case of nitrogen. Climate has more effect on assimilation than manures.

In the case of rye, as with other cereals, nitrogen has more influence than other manures, and a large supply of nitrogen in the soil is necessary during the period of greatest assimilation. This period varies greatly according to the season.

Nitrates should not be applied (for rye) in large quantities in the autumn, when the soil is light; ammoniacal or organic nitrogen is preferable. It is better to apply nitrogen in the spring and in the form of nitrate; and the application should be delayed if the spring is cold and wet. N. H. J. M.

Analytical Chemistry.

Auto-pneumatic Stirrer. By H. BREARLEY (*Chem. News*, 1896, **74**, 63).—In place of the mechanical stirrer employed to expedite the action of the solution on the metal when treating steels, &c., with copper ammonium chloride, it is suggested to cause air to bubble through the solution by means of an aspirator. The air should be washed by passing through a solution of lead acetate. D. A. L.

A Modified Form of Measuring Flask. By HEINRICH BILTZ (*Ber.*, 1896, **29**, 2082—2083).—The flask has a bulb blown on the neck between the mark and the stopper; the air in this bulb facilitates the thorough mixing of the liquid. In filling the flask it is advisable to use a funnel in order to avoid wetting the sides of the bulb. J. J. S.

Estimation of Hydrochloric acid in Gastric Juice. By WACŁAW VON MORACZEWSKI (*Chem. Centr.*, 1896, 667; from *Deutsch. med. Woch.*, **22**, 24—25).—The juice is evaporated down to 1 c.c., placed in a 100 c.c. flask, and a mixture of 25 c.c. of absolute alcohol and 75 c.c. of dry ether added to the mark. The whole is well mixed and allowed to remain; 50 c.c. of the mixture is then filtered into a larger flask, 50 c.c. of water, and a few c.c. of decinormal soda being added in order to neutralise it. It is then titrated with 1/50 normal silver nitrate solution, potassium chromate being used as indicator. After each addition of the silver solution, the flask is well shaken. Calcium and ammonium chloride, which are soluble in alcohol and ether, are present in negligible traces. The method gives the free acid *plus* that united to proteid. W. D. H.

Estimation of Sulphur in Cast-iron or Steel. By G. G. BOUCHER (*Chem. News*, 1896, **74**, 76).—Five grams of the iron or steel is dissolved in a strong solution of copper ammonium chloride; when the precipitated copper is dissolved, the solution is filtered, and the residue and paper, after washing free from copper with hot water, are boiled with about 30 c.c. of nitrohydrochloric acid or with bromine water and a few drops of hydrochloric acid. In the latter case, the excess of bromine is boiled off, the solution filtered, barium chloride added, and the barium sulphate collected, washed, ignited, and weighed. In the former case, the solution is filtered, neutralised with ammonia, slightly acidified with hydrochloric acid, treated with 5 grams of barium chloride, and so on. The results obtained with the process are satisfactory. D. A. L.

Estimation of Sulphur in Inorganic Sulphides. VI. By PAUL E. JANNASCH and O. HEIDENREICH (*Zeits. anorg. Chem.*, 1896, **12**, 358).—A sample of commercial mosaic gold (SnS_2) was analysed by heating 0.5 gram in a current of oxygen, and weighing the residual

dioxide. The escaping gases were passed through either 3—4 per cent. aqueous hydrogen peroxide, or very dilute hydrochloric acid and bromine, and the sulphuric acid formed was precipitated and weighed as barium sulphate. The chloride was determined by digestion with very dilute nitric acid and precipitation with silver nitrate. Result: Sn 64.69, S 33.07, Cl 0.38, H₂O (lost at 95°) 0.29; total 98.43. The deficit is caused by the presence of oxysulphide in the sample.

C. F. B.

Precipitation of Barium Sulphate by means of Barium Chloride. By GEORG LUNGE (*Zeits. angew. Chem.*, 1896, 453).—A reply to Gladding (this vol., ii, 622). There is no necessity for conducting the precipitation of barium sulphate as recommended by that chemist. Excess of barium chloride added all at once gives a sufficiently pure precipitate.

L. DE K.

Estimation of Sulphuric Anhydride in Fuming Sulphuric acid. Estimation of Sodium Sulphide. By PAUL DOBRINER and WILHELM SCHRANZ (*Zeits. angew. Chem.*, 1896, 453—456).—*Estimation of Sulphuric Anhydride.*—The following process is recommended. The sample is introduced in the well-known manner into a drawn-out weighing tube, which, after the point has been sealed, is re-weighed. The tube is then put into a stoppered flask containing about 150 c.c. of distilled water, and on thoroughly shaking so as to break the tube, the sulphuric acid is dissolved by the water. A weighed quantity of pure sodium carbonate is now added, so as to nearly neutralise the solution, which is then boiled to expel the carbonic anhydride. Phenolphthaleïn is added, and the neutralisation completed by means of accurate normal soda, of which about 3 or 4 c.c. at most should be required. If the total acidity calculated as SO₃ equals A per cent., the excess of SO₃ is found by making use of the formula $\frac{49}{9} A - 444.44$. The method of simply titrating with normal soda is scarcely accurate within 1 per cent.; the author's modification yields almost scientifically accurate results.

Assay of Sodium Sulphide.—(a) *Estimation of Sodium Sulphide in the Presence of Sodium Hydrosulphide.*—Twelve grams of the sample is dissolved and made up to a litre. 25 c.c. of this solution is delivered from a burette into 45 c.c. of N/20 iodine, previously mixed with 10 c.c. of normal sulphuric acid and diluted to 150 c.c. The yellow colour should completely disappear; if not, the experiment should be repeated with less iodine solution. After adding starch water, the small excess of liberated hydrogen sulphide is titrated by means of the same iodine solution, and the total amount of hydrogen sulphide is found by an easy calculation. 6 grams of the sample is dissolved in water, decomposed with a known excess of normal sulphuric acid, boiled to expel hydrogen sulphide, and titrated with normal soda using phenolphthaleïn as indicator. This gives the sodium sulphide, which is then calculated to hydrogen sulphide and deducted from the total hydrogen sulphide. The difference is due to hydrogen sulphide existing as 2NaHS. This is now recalculated to

Na_2S , and this being deducted from the sodium sulphide found, gives the real amount of the latter.

(b) *Estimation of Sodium Sulphide in the Presence of Sodium Hydroxide*.—If free alkali is present, the amount of hydrogen sulphide found will be insufficient to account for all the soda calculated as Na_2S . The excess of soda is then calculated to sodium hydroxide.

L. DE K.

Gravimetric Estimation of Selenium. By A. W. PEIRCE (*Zeits. anorg. Chem.*, 1896, 12, 409—412).—A portion of the sample containing from 0.2 to 0.4 gram of selenious anhydride is dissolved in hydrochloric acid, the solution, diluted to 400 c.c., is mixed with potassium iodide (the amount of which must be 3 grams in excess of the theoretical), and boiled for 10—20 minutes, until the red precipitate becomes black, and all free iodine is expelled. The precipitate is collected on an asbestos filter, washed, dried at 100° , and weighed. The results are fairly accurate, but always about 0.1 per cent. too high. It is essential that an excess of potassium iodide be employed, otherwise the precipitate will contain included iodine; also, the solution must be diluted before precipitation, or the precipitate will contain potassium iodide. If the selenium is present in a higher state of oxidation, the estimation is carried out in the same manner, but longer boiling is necessary. The method is very quick and convenient for determining the total percentage of selenium in a sample.

E. C. R.

Experiments on the Citrate-solubility of Basic Slags. By H. DUBBERS (*Zeits. angew. Chem.*, 1896, 468—473).—An exhaustive inquiry into Wagner's process. The author comes to the conclusion that the time of shaking with the ammonium citrate solution (half an hour) is quite insufficient, and that a larger quantity of acid ammonium citrate solution should be used. The author recommends using 500 c.c. of liquid, containing 10 grams of free citric acid and 5 grams of the same neutralised by ammonia. The shaking should be continued for about four hours.

L. DE K.

Iodometric Estimation of Carbonic acid. By J. K. PHELPS (*Zeits. anorg. Chem.*, 1896, 12, 431—435).—A weighed quantity of the carbonate is introduced into a flask connected with an absorption apparatus containing a solution of barium hydroxide; the apparatus is connected with an air pump, and the pressure diminished to 250—300 mm. The carbonate is then treated with a solution of phosphoric acid, previously boiled until free from carbonic anhydride, and the liberated carbonic anhydride is expelled into the absorption apparatus by five minutes boiling. The apparatus is cooled, and brought to atmospheric pressure, and the excess of barium hydroxide determined by adding an excess of iodine solution, boiling for a short time to decompose any hypoiodite which may be formed, and then determining the excess of iodine with a solution of arsenious acid. The solution containing the precipitated barium carbonate must be boiled before adding excess of iodine, as otherwise the iodine reacts slightly with the finely divided barium carbonate; after adding excess of iodine, the apparatus is connected with an absorption appa-

ratus containing potassium iodide, to arrest any iodine which may volatilise, and to exclude air. The method is accurate and expeditious; one estimation is easily performed in three-quarters of an hour.

E. C. R.

New Baryta Tube. By H. CHR. GEELMUYDEN (*Zeits. anal. Chem.*, 1896, **35**, 516—517).—When the carbonic anhydride in large volumes of air is to be estimated by Pettenkofer's method, the volume of the baryta solution may change during the absorption. A graduated baryta tube is therefore used, constructed on the pattern of a Gay-Lussac burette, but with the open end bent at a right angle to the main portion of the tube, which is laid in a nearly horizontal position whilst passing in the air through the narrow tube, but when raised into a vertical position allows the volume of the liquid to be read.

M. J. S.

Separation of Silver from Gold by Volatilisation. By JOSEPH W. RICHARDS (*Chem. News*, 1896, **74**, 2—3).—To separate silver from gold in assay buttons (obtained in the blowpipe assay), the button is supported in a hollow on a piece of dense charcoal, which must yield a white ash, and is exposed at an angle of 30° to a pointed needle-like oxidising flame directed downwards at an angle of 45° , precautions necessary to prevent displacement of the button by the blast. The button is heated at a redness, below the boiling point of silver, until it becomes brass-yellow, the temperature is then raised and taken almost to whiteness, when a gold colour is attained, this temperature being maintained until a distinct crimson coating is observed on the white ash; the amount of gold lost is negligible, but if the button is less than 0.25 mm. in diameter, a measured pure gold bead of almost equal size is added before the final stages of heating. The button is cupelled and measured.

D. A. L.

Estimation of Magnesia as Magnesium Pyrophosphate. By HUGO NEUBAUER (*Zeits. angew. Chem.*, 1896, 435—440).—The composition of magnesium ammonium phosphate does not seem to be quite so constant as was formerly believed, as the precipitate often contains excess of phosphoric acid, which may be expelled by a prolonged ignition. In other cases, there may be an excess of magnesia.

To obtain correct results, the sodium phosphate should be added at once, in large excess, to the ammoniacal magnesia solution; it is better still to add it to the acid solution, and then to add the ammonia. Excess of ammonium salts does not hurt, but in presence of much ammonium oxalate the precipitate must, after slight washing, be redissolved in hydrochloric acid, and reprecipitated with ammonia and some more sodium phosphate. The precipitate should be ignited over the blowpipe, or a powerful bunsen burner, for at least half an hour, and, after weighing, it should again be heated, to see if there is any further diminution in weight.

When dealing with small quantities of magnesia only, there is no need for these precautions, but if the amount is large they should not be neglected.

L. DE K.

Volumetric Estimation of Zinc by means of Potassium Ferrocyanide. By LUCIEN L. DE KONINCK and EUGENE PROST (*Zeits. angew. Chem.*, 1896, 460—468; 564—572).—The authors have made an exhaustive investigation as to the various reactions which take place when potassium ferrocyanide is added to a zinc solution. The reaction takes place somewhat slowly; therefore there may, at first, be an excess of ferrocyanide as proved by the uranium reaction. Soon, however, this excess disappears as an insoluble double compound of zinc and potassium ferrocyanide is formed. The direct titration of zinc by means of potassium ferrocyanide is, therefore, not to be recommended. The following process is found by the authors to give trustworthy results: 10 grams of pure zinc is dissolved in hydrochloric acid, nearly neutralised with soda, and made up to 1 litre. 27 grams of potassium ferrocyanide is dissolved in a litre of water. When checking, 20 c.c. of the zinc solution is mixed with 50 c.c. of a 20 per cent. solution of ammonium chloride, 2 drops of a 10 per cent. solution of sodium sulphite, and 10 c.c. of hydrochloric acid (sp. gr., 1.075); the zinc solution must be measured from an accurate pipette, but the others are only roughly measured. 40 c.c. exactly of the ferrocyanide solution is now added, and, after being left for at least 10 minutes, the excess is titrated with the zinc solution until the uranium reaction is no longer obtained. The relation between the zinc and the ferrocyanide is thus determined.

The estimation of zinc in any of its ores is now very simple. 2.5 grams of the sample is dissolved in nitrohydrochloric acid and evaporated to dryness to render any silica insoluble, the residue being taken up with 5 c.c. of hydrochloric acid and a little water. The filtrate is freed from lead, cadmium, &c., by a current of hydrogen sulphide, boiled to expel the gas, and, after cooling, mixed with 25 c.c. of saturated bromine water. After pouring the liquid into a 500 c.c. flask, containing 100 c.c. of strong ammonia and 10 c.c. of a 25 per cent. solution of ammonium hydrogen carbonate, it is, when cold, made up to the mark.

When the precipitate has quite settled, the liquid is passed through a dry filter. 100 c.c. is then pipetted off, acidified with hydrochloric acid, and titrated with the ferrocyanide in the way described. L. DE K.

Separation of Mercury from Arsenic, Antimony, and Copper by Ignition in a Current of Oxygen. By PAUL E. JANNASCH (*Zeits. anorg. Chem.*, 1896, 12, 359—364; compare this vol., ii, 546).—Mercury can be separated from antimony by oxidising the mixed sulphides with fuming nitric acid, driving off the excess of acid by heating first at 90—100°, then at 150—180°, in a current of air or carbonic anhydride, and finally igniting in a current of oxygen. The antimony remains as the oxide, Sb_2O_3 , and is weighed as such. The mercury that volatilises is collected in vessels containing dilute nitric acid, and is estimated as described previously; the addition of a little hydrogen peroxide promotes the solution of the metal in the acid.

Mercury can be separated from copper by igniting the mixed sul-

phides in a current of oxygen. The mercury volatilises, and is collected in vessels containing dilute nitric acid and bromine water; the solution is evaporated almost to dryness, the residues treated with hydrochloric acid and water, and the mercury precipitated and weighed as sulphide. The copper remains in the vessel as oxide after the ignition, and may be weighed as such, or it may be dissolved in acid and precipitated with sodium hydroxide.

Mercury can be separated from arsenic by evaporating the solution in nitric acid, moistening the residue with water, and adding a little pure magnesia, drying at 180° , and then igniting in a current of oxygen. The mercury volatilises and is collected in vessels containing dilute nitric acid and hydrogen peroxide, and estimated in the solution thus obtained. The residue is dissolved in strong hydrochloric acid, some citric acid is then added, and a large excess of ammonia; the precipitate which forms is converted into magnesium pyroarsenate, and weighed as such.

C. F. B.

Estimation of Nickel in Steel, &c. By H. BREARLEY (*Chem. News*, 1896, **74**, 16--17).—A gram of steel is dissolved in 20 c.c. of nitric acid (sp. gr., 1.2), in a 1100 c.c. beaker, cooled, treated with dilute ammonia to slight precipitation, then with hydrochloric acid until again clear; to this are added 70 c.c. of strong acetic acid, 950 c.c. or so of hot water, and 50 to 70 c.c. of ammonium acetate made by neutralising acetic acid with ammonia. The whole is boiled and made up to a litre, and half this is filtered hot, cooled, rendered alkaline with ammonia, and mixed with 2 c.c. of a solution containing 20 grams of potassium iodide per litre, and 2 c.c. of a solution containing 2.5 grams of silver nitrate per litre; a solution of potassium cyanide (4.5 grams per litre, and standardised against standard nickel) is then run in until the silver iodide dissolves and the solution is clear. Tungsten and manganese do not interfere, and the coloration, due to chromium, is overcome by boiling the iron precipitate for half an hour. Copper has to be separated from the solution containing it and the nickel by means of sulphurous acid and thiocyanate.

With regard to procedure, adding the acetate to the hot solution is advantageous, since, in the presence of 70 to 100 c.c. of acetic acid, the precipitate does not appear before $85-90^{\circ}$, but immediate precipitation should be avoided, as it causes low results. For filtering, fibrous asbestos, on a perforated plate $1\frac{1}{2}$ inch in diameter, is found expedient; the tip of the funnel used must be flat, and until in use the space below the perforated plate must be kept full of water, which is completely displaced by the first 300 c.c. of solution.

D. A. L.

Standardisation of Permanganate. By E. RIEGLER (*Zeit. anal. Chem.*, 1896, **35**, 522).—The chief objection to keeping a standard solution of oxalic acid in readiness for the titration of permanganate is that it does not remain unaltered in strength. This may be overcome by the addition of a sufficient quantity of sulphuric acid. A solution containing 9.9654 grams of oxalic acid and 50 c.c. of concentrated sulphuric acid in the litre underwent no change in strength in the course of a year.

M. J. S.

Examination of Commercial Thorium Nitrate and Separation of Thorium from Cerium. By C. REMIGIUS FRESENIUS and E. HINTZ (*Zeits. anal. Chem.*, 1896, **35**, 525—544).—The authors having analysed, by methods which they propose to publish later, 11 specimens of mantles for incandescent gas illumination, produced by different makers between March and October, 1895, in which thorium and cerium oxides were the principal constituents, were further required to give an opinion whether the cerium oxide present might be regarded as an impurity resulting from the methods of manufacture in use at that time, or had been intentionally added. The percentage of cerium oxide found in the mantles ranged from 0·38 to 2·02 (average 1 per cent.). Having obtained three samples of thorium nitrate which had been sent into the market during the period in question, one of which had been prepared from monazite, which contains only 4—5 per cent. of thoria, with 50—60 per cent. of oxides of the cerium metals, the percentage of cerium was estimated as follows. The dilute solution (1 per cent. or less) of the nitrate was precipitated by boiling with thiosulphate, and the precipitate dissolved in hydrochloric acid and thrown down by ammonia. The original filtrate was also precipitated by ammonia. The two precipitates were dissolved in hydrochloric acid and both solutions again submitted to the thiosulphate precipitation, this treatment being repeated several times. Finally, the ammonia precipitate from the filtrates was dissolved in nitric acid, and, after driving off the excess of acid, the cerium, yttrium, lanthanum, and neodymium were precipitated by oxalic acid. The ignited precipitate was fused with potassium hydrogen sulphate, again precipitated by ammonia, and dissolved in hydrochloric acid. Cerium was now thrown down alone by the addition of sodium acetate and hypochlorite, this precipitation being repeated a second time. Lastly, the oxide was dissolved in nitric acid, thrown down by ammonia, washed, ignited, and weighed. Yttrium and neodymium (including lanthanum) were separated by saturated potassium sulphate solution. Thorium was in all cases found by difference. The cerium oxide found in the three samples was 0·186, 0·0463, and 0·202 per 100 parts of total oxides, and, since the highest of these is only about one-half of the lowest amount, or one-fifth of the average amount, found in the mantles, the authors conclude that the cerium oxide there present had either been purposely added, or resulted from the use of a thorium salt of less purity than was commercially attainable at that time. As a further proof that the methods known to chemists in 1895 were capable of effecting a far greater degree of separation than was found in the mantles, mixtures of cerium and thorium salts were prepared, containing respectively 2·02 and 0·38 per cent. of cerium oxide. By three precipitations with thiosulphate, and a subsequent precipitation by oxalic acid, there were recovered 98 and 96·6 per cent. of the cerium taken, the precipitates containing only 0·7 and 0·3 per cent. of thoria respectively.

M. J. S.

Separation of Bismuth from the Metals of the Copper and Iron Groups by heating their Salts in a Current of dry Hydrogen Chloride. By PAUL E. JANNASCH and S. GROSSE (*Zeits.*

anorg. Chem., 1896, **12**, 398).—Bismuth, like tin (*Abstr.*, 1895, ii, 462), volatilises under these circumstances at a comparatively low temperature, and so can be separated from metals the chlorides of which are less volatile. C. F. B.

Estimation of Ethylene in Gaseous Mixtures. By P. FRITZSCHE (*Zeits. angew. Chem.*, 1896, 456—459).—The process is based on the fact that ethylene is completely absorbed by strong sulphuric acid, and that this solution, when diluted with twice its bulk of water and submitted to distillation, yields the quantitative amount of alcohol.

When operating on mixtures rich in ethylene, the process scarcely gives any trouble, but when the gas is present in traces only it is not so simple. In this case, a large quantity of the gaseous mixture is introduced in a glass apparatus containing a little sulphuric acid, which is continually allowed to run over the sides, so as to offer a large surface to the gas. To accelerate the absorption, the apparatus is heated in an air bath at 100°. After diluting the acid and distilling, the distillate is neutralised with soda and again submitted to distillation; this has to be repeated until the amount of alcohol reaches about 1—2 per cent. It is then estimated, as usual, by taking the specific gravity of the liquid.

Any butylene may be first separated from the ethylene by the action of sulphuric acid of 70 per cent., which does not affect the ethylene. Experiments conducted with the idea of converting the ethylene into ethylic barium sulphate, and estimating this volumetrically, have not, as yet, yielded satisfactory results. L. DE K.

Estimation of Essential Oil of Mustard in Feeding Cakes. By MAX PASSON (*Zeits. angew. Chem.*, 1896, 422—423).—Twenty-five grams of the sample is introduced into a flask containing 300 c.c. of water and 0.5 gram of tartaric acid. The flask, which is provided with a safety tube, is connected with a smaller flask containing 75 c.c. of glacial acetic acid and a little zinc and iron dust, to effect a partial reduction of the ethereal oil. To prevent any escape of the latter, the second flask is fitted with a bent tube dipping into sulphuric acid contained in a beaker.

The mixture is slowly distilled for about two hours, and then the acetic and sulphuric acids are mixed. An aliquot part of the mixture is boiled with an equal bulk of sulphuric acid and a drop of mercury to convert the nitrogen into ammonia, which is then estimated as usual.

One c.c. of N/10 soda represents 0.0099 gram of essential oil of mustard (allylthiocarbimide). Test experiments with small quantities of the pure oil were quite satisfactory. L. DE K.

Estimation of Sugar in Blood. By E. WAYMOUTH REID (*J. Physiol.*, 1896, **20**, 316—321).—In the method described, phosphotungstic acid is used as the precipitant for proteid; this is filtered off and washed by the use of a filter plate, and the sugar estimated by

the Allihn-Soxhlet gravimetric process. The results obtained show that the method is both accurate and rapid. W. D. H.

Messinger's Method of Estimating Acetone. By H. CHR. GEELMUYDEN (*Zeits. anal. Chem.*, 1896, **35**, 503—516).—The author, desiring to employ Messinger's method (*Abstr.*, 1889, 313; 1891, 370) for the estimation of acetone in the breath of animals and in urine, examined by means of test-analyses the influence of the various modifications which the circumstances necessitated. Collischonn's statement that a mixture of iodine and alkali hydroxide soon loses the power of converting acetone into iodoform is amply confirmed. Such a solution cannot, therefore, be employed for absorbing acetone from the products of respiration. By passing the gases through strong potash alone, all the carbonic anhydride and part of the acetone were absorbed. The gases were then conducted over ignited cupric oxide, and the carbonic anhydride produced was absorbed in a special form of Pettenkofer's tube (see this vol., ii, 674). Blank experiments showed that the air from the lungs of animals contained no other volatile organic substance, and test experiments in which known quantities of acetone were volatilised in the empty live cage yielded results within 10 per cent. of the truth. Since this method required the use of very strong potash solution (40 per cent.), the influence of this high strength on the estimation was examined, and it was found that no loss of acetone occurred when it was kept dissolved in such potash for 24 hours before titration, but that it was necessary to dilute the solution with 2—3 vols. of water before adding iodine, otherwise the formation of iodoform was so instantaneous that some iodine became enclosed. In carrying out the Messinger-Huppert method for estimation in urine, some loss is inevitable; this amounted on an average to 6.75 per cent. when the distillate was cooled with ice, and to 8.3 per cent. when water of a few degrees above zero was used. Acetone solutions of very low temperature do not, however, react completely with iodine, especially when the alkali present is greatly diluted. The temperature should, therefore, be raised to 18—20° by addition of hot water or hot potash just before the iodine. The distillation should be carried nearly to dryness, the end of the condenser tube dipping into the potash in the receiver. A small correction is required for some volatile substance which distils from normal urine and consumes iodine, although it produces no iodoform. In human urine, amounts varying from 0.58 to 1.35 (calculated as milligrams of acetone) per 100 c.c. were found. The addition of urea should be avoided, unless nitrites are present, since it lowers an already deficient yield. M. J. S.

Examination of Oil of Bergamot. By ARTHUR BORNTÄGER (*Zeits. anal. Chem.*, 1896, **35**, 523—525).—The discrepancy between the percentages of linalyl acetate found by Schimmel and Co., and the author respectively (this vol., ii, 228) seems to have been due to differences in the ripeness of the fruit from which the oil was obtained. Five samples of oil prepared by simple pressure from sound, ripe fruit gave the limits 38.5—42 per cent. Later estima-

tions by Schimmel and Co. in last seasons oil have given an average of 37 per cent., the oil from unripe fruit showing only 33—34 per cent., and a few specimens towards the close of the season exhibiting 40 per cent. and upwards (44 per cent.). The product of the season was, however, of low quality. M. J. S.

Simple Process for Testing Linseed Oil, Boiled Oil, and Paints. By RUDOLF HEFELMANN and PAUL MANN (*Chem. Centr.*, 1896, i, 133; from *Pharm. Central-Hall.*, 36, 685—688).—The chief adulteration practised is the addition of rosin oil, rosin, or rosin soap; mineral oil is also frequently used. The authors find that these frauds may be readily detected by the butyro-refractometer. Pure oil and boiled oil, which at 25° give a refraction of 80—84.5, show, on mixing with 20 per cent. of rosin or rosin oil, a refraction above 100. Mineral oils also cause a higher refraction. The polariscope may also be used, as rosin oil will cause a strong right-handed, and rosin, a slight right-handed polarisation, whilst mineral oil causes a slight left-handed polarisation. The experiment is carried out by shaking 15 c.c. of the sample with 15 c.c. of absolute alcohol; the alcoholic layer is poured off, mixed with a little chloroform, filtered, and then polarised. When testing paints, 2—5 grams of the sample is treated with 20 c.c. of light petroleum, and, after whirling in a centrifugal apparatus, the liquid is poured off, evaporated, and the oil, after drying at 100°, is tested in the refractometer. L. DE K.

Iodine Number of Pure and Boiled Linseed Oil. By ALEXANDER KATZ (*Chem. Centr.*, 1895, ii, 463; from *Forsch. Ber. Lebensm. Hygiene*, 2, 203—204).—The iodine number depends on the time during which the Hübl solution is allowed to act, but remains constant after 24 hours. The action should be allowed to take place in the dark. The average iodine number of raw linseed oil is 182; that of boiled oil 173. L. DE K.

Iodine Number of Cacao Butter. By F. FILSINGER (*Zeit. anal. Chem.*, 1896, 35, 517—521).—The wide limits, 32.8 to 41.7, assigned by Strohl (this vol., ii, 506) induced the author to recall the results obtained in 1889 by himself and Henking in the examination of all the varieties of raw cacao in use in Germany, 18 in number (compare *Abstr.*, 1891, 869). All the results lay between 33.4 and 37.5, and these limits have been fully confirmed by more recent experience. It is suggested that the fat in Strohl's specimens, some of which were several years old, may have become decomposed with liberation of free acids, which, as is well-known, absorb more iodine than the neutral fats. Strohl's samples having been wholly consumed, no re-examination is possible. M. J. S.

Extracting Fat from Cheese for Testing Purposes. By OTTO HENZOLD (*Chem. Centr.*, 1896, i, 140—141; from *Milch Zeit.*, 24, 729—730).—Three hundred grams of the sample of cheese, cut up into little dice, is shaken in a wide necked flask with 700 c.c. of

5 per cent. aqueous potash heated to 22°. After about 10 minutes, the casein has dissolved, and the fat floats on the surface. It is then removed, washed, melted, filtered through a small filter, and submitted to the usual tests.

L. DE K.

New Method for Quantitative Isolation of Alkaloids. By KARL KIPPENBERGER (*Zeit. anal. Chem.*, 1896, 35, 407—421).—In continuation of his work on the detection of poisonous alkaloids in cadaveric matter (*Abstr.*, 1895, ii, 465; this vol., 282), the author has developed a method of obtaining the pure alkaloids from their periodides. He first shows that by precipitating neutral, or feebly alkaline solutions with the iodine reagent, the precipitate is free from ptomaines or other normal constituents of an extract of cadaveric matter. Having, therefore, obtained an extract which may contain these substances, it is acidified and heated to coagulate albumin, then neutralised or rendered feebly alkaline, and precipitated by an iodine solution containing 12·7 grams of iodine and 60 grams of potassium iodide per litre. The precipitate is collected on an asbestos filter, washed thoroughly with cold water, and dissolved in a small quantity of purified acetone, in which menstruum all the alkaloid periodides are freely soluble. On treating the acetone solution with an alkaline hydroxide, and then acidifying with hydrochloric acid, the alkaloid is converted into its hydrochloride, with liberation of iodine, the latter, after warming to expel acetone, being removed by the addition of thiosulphate. Excess of sodium carbonate is then added, and the alkaloid extracted by shaking with chloroform (in some cases a mixture of chloroform and ether; in others, morphine and narceine, chloroform and alcohol). The chloroform solution leaves the pure alkaloid on evaporation, but as an uncertain amount of water of crystallisation may be present in the residue, the weight requires to be confirmed by some form of titration (see next abstract, also 1895, ii, 467). The behaviour of morphine is peculiar. On gradually adding the iodine solution to a morphine salt supersaturated with alkali, a grass-green colour is obtained before any precipitate is produced. This seems to be due to a partial oxidation of the morphine to oxydimorphine, and is characteristic of that alkaloid.

A similar method can be applied to the preparation of the pure alkaloids from plant extracts. After treating the acetone solution with alkali and acid as above, and before adding thiosulphate, the whole is shaken with petroleum, of boiling point 30—50°, by which certain impurities are removed. This branch of the subject the author proposes to study more minutely.

The tendency, which most alkaloids exhibit, to turn brownish when their ethereal solutions are evaporated and the residue is dried on the water bath, can be completely counteracted by the presence of a little alkali carbonate, and the trace of this salt, which ether is capable of dissolving, suffices for the purpose. Sodium carbonate is, therefore, to be preferred to ammonia for the liberation of an alkaloid from its salts.

A common method for recovering an alkaloid from its ethereal solution is to convert it into a salt by adding an acid, but since the

ethereal solutions obtained from cadaveric matter are very liable to contain ammonia, as well as amido-bases and acids, the salts of these substances separate simultaneously. As, however, none of these give precipitates with iodine, the use of the iodine method is here very advantageous.

M. J. S.

Titration of Alkaloids by Iodine Solution. III. By KARL KIPPENBERGER (*Zeit. anal. Chem.*, 1896, **35**, 422—471).—As indicated in the earlier papers on this subject (*Abstr.*, 1895, ii, 467; this vol., 282) the amount of free iodine consumed, when a solution of iodine in potassium iodide reacts with a salt of an alkaloid to form periodide, is always greater than corresponds with the equation $\text{Alk.HCl} + \text{KI} + \text{I}_2 = \text{Alk.IH.I}_2 + \text{KCl}$, and varies considerably not only with the different alkaloids, but with varying conditions of the experiment. Attempts to produce the alkaloid hydriodides by treating the hydrochlorides (or sulphates) with various metallic iodides (ammonium, magnesium, or barium), either before, or simultaneously with the addition of the iodine reagent, led to no greater uniformity in the results, and the same was the case when the amount of free acid (whether hydrochloric, hydrobromic, or hydriodic) in the alkaloid solution was increased. The addition of haloïd salts had in general the same effect, although with brucine the addition of a considerable amount of potassium iodide, or with morphine, of bromide, reduced the amount of iodine consumed to the theoretical 2 atoms. Finally, however, the following method was found to be applicable to all the alkaloids examined (brucine, morphine, atropine, narcotine, quinine). The alkaloid is dissolved in the smallest possible excess of a standard acid (hydrochloric or sulphuric) avoiding dilution as far as possible. There is then added a solution of silver iodide in potassium iodide prepared by dissolving 1 gram of silver nitrate, and 10 grams of potassium iodide in 20 c.c., and employing only so much of this reagent as is exactly equivalent to (or very slightly in excess of) the acid used. Thus, for 0.1 gram of hydrogen chloride there would be used $20 \times 0.1 \times 170/36.5 = 9.32$ or 9.4 c.c. Should a greater excess of the silver solution have been added, and a double salt of the alkaloid and silver have thereby been precipitated, this injurious effect can be counteracted by adding more potassium iodide, and waiting until the precipitate is redissolved. Iodine solution (N/20) is then added in the smallest possible excess. The formation of the alkaloid periodide is complete in 2—3 minutes. The liquid is poured through an asbestos filter, and the excess of iodine in an aliquot part of the filtrate is estimated by N/20 thiosulphate. Using thiosulphate of this strength, there is no risk of forming silver thiosulphate. One molecule of alkaloid consumes exactly 2 atoms of iodine, except in the case of quinine, where the tendency to the formation of diacid salts is exemplified by the consumption of 4 atoms.

M. J. S.

Testing Cinchona Extract. By MARIUS L. Q. VAN LERDEN HULSEBOSCH (*Chem. Centr.*, 1896, i, 141—142; from *Ber. pharm. Ges.*, 1895, 286).—One gram of the sample is dissolved in a small beaker in 5 c.c.

of water and 5 drops of normal hydrochloric acid. After pouring it into the author's extraction apparatus, which is a kind of Soxhlet's tube, the beaker is rinsed twice with 5 c.c. of water, and the liquid is then extracted with ether for an hour. After adding 2 c.c. of normal soda to liberate the alkaloids, the extraction is repeated, and, after evaporating off the ether in a tared flask, the alkaloids are dried at 100° and weighed.

To estimate the amount of cinchona tannates, 10 grams of the liquid extract is introduced into a tared narrow beaker, and mixed with 10 c.c. of a 20 per cent. solution of sodium acetate. The turbid mixture is heated on the water bath until the tannate has agglomerated and coated the sides of the beaker. The liquid is poured off, the deposit washed with a very little water, dried at 100° , and weighed.

L. DE K.

Reactions of Digitalin. By C. C. KELLER (*Chem. Centr.*, 1896, i, 132; from *Ber. pharm. Ges.*, 1895, 275).—Commercial digitalin contains four active constituents: Digitonin, a glucoside yielding, on hydrolysis, digitogenin, glucose, and digitalose; digitalein, an amorphous glucoside, yielding digitaligenin, glucose, and digitalose; digitalein, a crystallised glucoside, yielding products not yet investigated, and digitoxin, a bitter principle. The author has discovered delicate colour reactions for these four substances. The sample is dissolved in 3–4 c.c. of glacial acetic acid, a drop of dilute ferric chloride is added and then an equal bulk of sulphuric acid, without shaking. The colour generated at the place where the two layers touch is carefully observed. Digitonin gives a faint rose-red, evanescent, colour. Digitalin gives a bright carmine-red colour, very permanent, still visible with 0.05 milligram per c.c. Digitalein gives a similar colour but less distinct and not so permanent. The test with digitoxin is very characteristic. The result is a dirty bluish-green ring, which soon breaks up into two layers, the bottom one of which is brownish-red, whilst the top assumes an indigo-blue colour.

L. DE K.

Chemical Examination of Cheese. By ALBERT STUTZER (*Zeit. anal. Chem.*, 1896, 35, 493–502).—For all the estimations, except that of ash, a mixture should be prepared by triturating the cheese with four times (or in the case of soft cheese, five times) its weight of washed, ignited, and sifted quartz sand. The ash, water, fat, and total nitrogen are estimated by the usual processes of incineration, drying at 100° , extracting the dried residue with ether, and the Kjeldahl process respectively. For the distillation of the ammonia, barium carbonate is a safer form of alkali than magnesia or magnesium carbonate. Nitrogenous compounds (other than ammonia), which are not precipitable by phosphomolybdic acid from a cold, aqueous extract of the cheese, are set down as amides. For experiments on the digestibility of cheese, a stock of pepsin solution is prepared as follows:—The mucous membranes of six fresh pig's stomachs are cut up small, and extracted for 24 hours with 30 litres

of 0.2 per cent. hydrochloric acid, 15 grams of thymol, dissolved in alcohol, being added as a preservative. The liquid is then strained (without squeezing) through a flannel bag, and filtered, first through loose, then through dense, filter paper. It retains its activity for several months. To estimate the total digestible constituents, a quantity of the sand mixture containing 5 grams of cheese is freed from fat by ether, and then digested for 48 hours at 37–40° with 500 c.c. of this extract, adding every two hours 5 c.c. of 10 per cent. hydrochloric acid until a total acidity of 1 per cent. is reached. The indigestible residue is then collected on an asbestos filter, and its nitrogen estimated. For albumose and peptone, the cheese is exhausted by boiling with 100 parts of water (in five portions), and one part of the cooled and filtered extract is acidified with sulphuric acid, and precipitated by phosphomolybdic acid. Another part of the extract is concentrated and saturated with zinc sulphate (see this vol., ii, 83), and the filtrate is tested for pancreas peptone by adding strong soda solution until the zinc oxide is redissolved, and then a few drops of 1 per cent. copper sulphate solution (the biuret reaction). The amount of peptone is calculated from the difference between the nitrogen in the phosphomolybdic and zinc sulphate precipitates. Deducting the soluble and the indigestible nitrogen from the total nitrogen, the remainder gives the casein and albuminates, or these may be directly, but less conveniently, estimated in the residue of the extraction with hot water. It is advisable further to estimate the digestibility of the cheese by submitting it to a process of interrupted digestion. A quantity of the sand mixture (in this case not freed from fat), containing 0.15 gram of nitrogen in the form of insoluble, but digestible casein and albumin, is treated with 150 c.c. of the pepsin solution and 350 c.c. of water containing 0.7 gram of hydrochloric acid, both liquids being warmed to 40° before adding, and the mixture being maintained at the same temperature for 30 or 60 minutes, stirring every five minutes. At the end of the given period, the whole is poured into two large, rapid, ribbed filters, and a portion of the filtrate collected in the first five minutes is used for the nitrogen determination.

M. J. S.

ERRATA.

VOL. LXII (ABSTR., 1892).

Page	Line	
420	18	for "Brandite" read "Brandtite."
585	4	„ "cyanide" read "oxide."

VOL. LXIV (ABSTR., 1893).

PART I.

124	top	„ "Acid" read "Action."
280	2	„ " $\text{C}_6\text{H}_4\langle\underset{\text{N}}{\text{C}(\text{COOH})}\rangle\text{N}$ " read " $\text{C}_6\text{H}_4\langle\underset{\text{N}}{\text{C}(\text{COOH})}\rangle\text{NH}$."
610	8	„ "1892" read "1891."

VOL. LXIV (ABSTR., 1893). *

PART II.

285	2*	„ "C" read "Cu."
382	2	„ "Sundite" read "Sundtite."
„	11	„ " $(\text{Ag}_2\text{Cu}_2\text{Fe})\text{S}, \text{Sb}_2\text{S}_3$ " read " $(\text{Ag}_2\text{Cu}_2\text{Fe})\text{S}, \text{Sb}_2\text{S}_5$."

VOL. LXVI (ABSTR., 1894).

INDEX.

519	4, col. ii,	for "animal" read "vegetable."
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* From bottom.

VOL. LXVIII (ABSTR., 1895).

PART II.

Page	Line	
172	17	for "K. KOSMAN" read "HANS BERNHARD KOSMANN."
222	10*	" "silver iodide" read "silver sulphide."
505	2	" "tetartohedral" read "tetrahedral."

INDEX.

573	15, col. i, for "439" read "449."
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VOL. LXX (ABSTR., 1896).

PART I.

16	25	for "211.5—212.5°" read "189.5—190°"
"	28	" "189.5—190°" " "211.5—212.5°"
26	10, 11	" "orthotolueneorthoeresetol" read "orthotolueneazoortho- eresetol."
27	9,* 8*	" "metaphenetoilparaphenetoil" " "metaphenetoilazo- paraphenetoil."
43	4,* 3*	" "2:3-diethoxybenzoylformic" " "2:4-diethoxybenzoyl- formic."
52	12, 13	" "2:7:2':7'-tetramethylxanthylene" read "2:7:2':7'- tetramethyldixanthylene."
89	6	" "NO ₂ ·CH(COOH) ₂ " read "NO ₂ ·CH(CONH ₂) ₂ ."
147	10*	" "574" read "653."
"	4*	" "C ₆ H ₃ (NO ₂) ₃ " read "C ₆ H ₃ (NO ₂) ₃ ."
235	16*	" "methylphenylhydrazinesulphonate" read "phenylmethylhydra- zinesulphamate."
343	18*	" "thiosulphochloride" read "thiochloride."
401	5*	" "CMe ₂ ·CBr·CHMeBr" " "CMe ₂ Br·CHMeBr."
425	11*	" "one ethylic union" read "one ethylenic union."
434	13* & 10*	" "Trimethylphenylacetic acid" read "Trimethylphenylgly- collic acid."
436	6	" "Benzylidenemethylhydrazine" " "Phenylbenzylidene- methylhydrazine."
478	16*	" "NPh ₁ ·CH·NH·C ₆ H ₃ Cl ₂ " read "NPh ₁ ·CH·NH·C ₆ H ₃ Cl ₂ ."
531	14*	" "2:4:2-bromiodinitrotoluene" read "2:4:6-bromiodo- nitrotoluene."
547	23	" "Hemellitene" read "Hemimellitene."
548	5	" "NH ₂ :NH·NHCONH ₂ :COOH" read "NH ₂ :NH·CONH ₂ :COOH."
673	4*	" "CHMe ₂ ·CH ₂ ·CH ₂ ·CH(NO ₂)·[CH ₂] ₃ ·CHMe ₂ " read "CHMe ₂ ·CH ₂ ·CH(NO ₂)·[CH ₂] ₃ ·CHMe ₂ ."
686	17	delete "C ₁₃ H ₁₆ N ₂ S ₂ O ₄ ."

Page Line

- 693 15-29 The constitution assigned to the two naphthylenediaminedisulphonic acids should be reversed, the authors having described the 1 : 3' . . . 3 : 1'-acid as 1 : 3' . . . 4 : 1', and *vice versa*.

VOL. LXX (ABSTR., 1896).

PART II.

- 36 20* for "Ca" read "CaO."
 37 2 " "T. E. WOLFF" read "JOHN E. WOLFF."
 110 bottom " "Mauzelins" read "Mauzelius."
 197 23 " "SEBELLIEN" " "SEBELLIEN."
 371 22 " "Przibram" " "Przibram."
 374 17 after "**Hornblende**" insert "**Hastingsite**."
 480 7 for "FEDERICO SHICKENDANTZ" read "FEDERICO SCHICKENDANTZ."
 586 10* " "Dumortierite" read "Dumortierite."
 596 10* }
 597 3 & 20 } " "JOHN NORMAN LOCKYER," read "JOSEPH NORMAN LOCKYER."
 655 25 " "Water" read "Waters."
 " 26 " "1895" read "1896."
 " 18* " "mineral" read "rock."
 659 6 " "by" read "and."

INDEX.

- Page col. .
 699 1 insert **Dixon**, *Augustus Edward*; thiocarbimides derived from complex fatty acids, T., 1593; P., **1896**, 223.
 708 2 " **Hada**, *Seihachi*, how mercurous and mercuric salts change into each other, T., 1667; P., **1896**, 182.
 724 2 for "**Luxmore**" read "**Luxmoore**."
 898 2 15* 14* for "*d*-iso-Propylpropane dd_1d_1 -tricarboxylic" read *a* iso-Propylpropane aa_1a_1 -tricarboxylic."
 929 2 top line delete "salts," after "Magnesium."
 990 1 3 after "Propionic acid" insert " β -iodo-."

* From bottom.